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Water Chemistry

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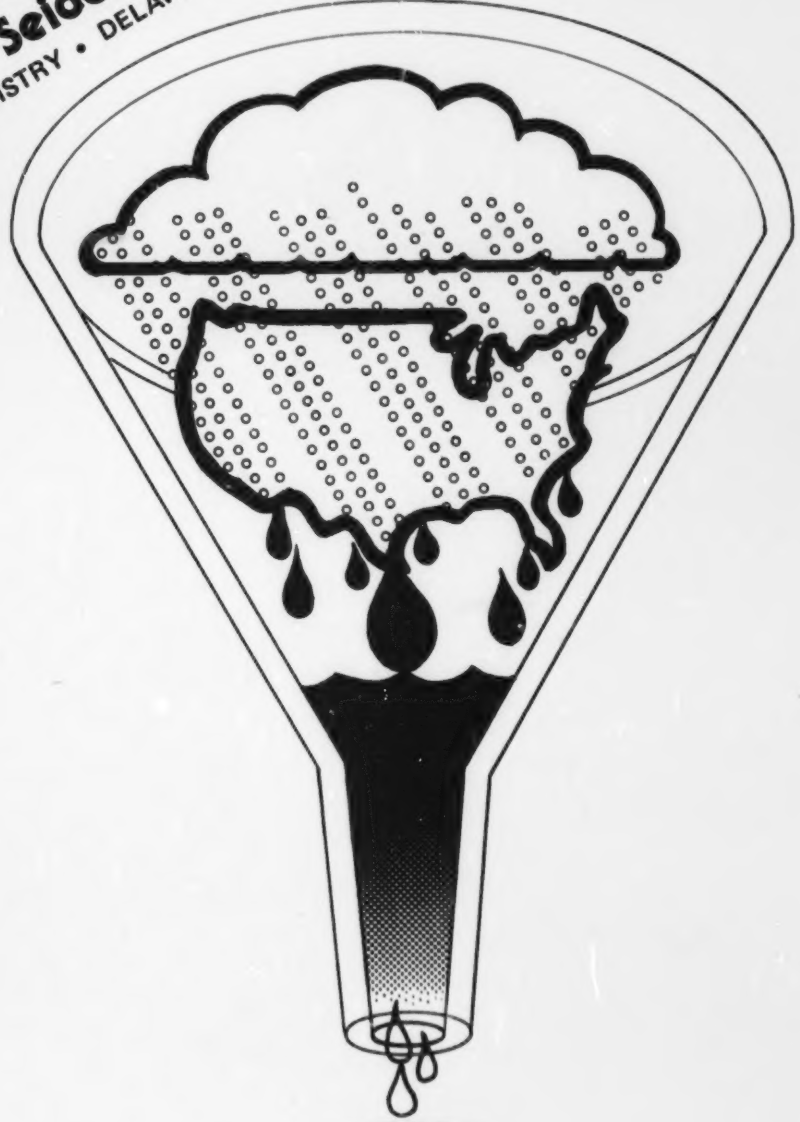

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THIS GOOD EARTH

Teachers and counselors have long since recognized that students must be motivated if they are to achieve their best results in any given area of study. How to involve them and what incentives to set before them are challenges to any conscientious teacher at every level of the educational process. If the terms are new, the idea is ancient for it was said long ago that a man must lose his life in order to find it. Perhaps no greater scientific challenge has ever faced the embryonic chemist, biologist, marine biologist, ecologist - just to mention a few - than the preservation of a healthy environment on this good earth.

Americans in particular have taken far too much for granted regarding the marvelous piece of real estate we call our own. We are blessed with vast resources of rich mines; fertile fields; great forests; hills and mountains for the storage of water as well as for their beauty and buried treasures. Innumberable streams, rivers and lakes feed two great oceans which in many areas, are supplemented with vital tidal marshes. Perhaps no one commodity is more important to life on this good earth than clean and abundant water. Civilization puts an unusually heavy demand upon this all important chemical compound; it therefore follows that the industry, commerce, agriculture, recreation, and urbanization of the United States has created an extremely crucial water problem that must be solved - or else.

This is not to say that other nations do not face equally serious or perhaps more serious water crisis than we do, but it is no comfort to anyone that misery likes company. Environmentalists are telling us with ever more alarm that all people are in the same boat together, and that boat is the heavenly body we call this good earth. Americans are being told with more and more controls and warnings that we can no longer be prodigal with our waste water, waste gases and solid wastes. There may have been a time when this country was young and unspoiled that the few people here could dump their sewage in a near-by stream, their factory smoke into the atmosphere and their garbage into a convenient ditch. Those days are gone forever, but satisfactory answers are not forthcoming as fast as they are needed.

To better understand our plight and to grasp some measure of what must be done, let us try to appreciate what a truly marvelous and unique planet is our good earth. As noted in the acknowledgment, almost all of the remainder of this chapter is taken from an address given by Dr. William G. Pollard, Executive Director of the Associated Universities of Oak Ridge, Tennessee.

Our sun and its planets were formed four and a half billion years ago by gravitational condensation from a cloud of gas and dust; all of the planets, in addition to their present solid cores, had dense atmospheres of hydrogen, helium, ammonia, methane, and water gases. This was so because hydrogen and helium are universally still by far the most abundant elements in the universe. Next in abundance are carbon, nitrogen, and oxygen. Most of the carbon and nitrogen united with hydrogen to form methane and ammonia. The oxygen was tied up in water, carbon dioxide, and in various solid oxides in the rocks which contained much water tied up with them as water of crystallization.

The very large planets such as Jupiter and Saturn still retain this original atmosphere. The smaller and warmer planets - Mars, Earth, Venus, and Mercury - lost this atmosphere at differrates during the first one to three billion years of their histories. The intense ultra-violet radiation from the sun was absorbed in the upper layers of the atmosphere and broke hydrogen atoms away from ammonia, methane, and water molecules. The hydrogen thus released escaped into space, along with helium, because the gravitational attraction of these smaller planets was not sufficient to hold these fast moving light atoms. The nitrogen left behind from the ammonia formed a residual atmosphere of nitrogen (N_2) and the carbon left behind from the methane united with oxygen released from water to greatly augment the original carbon dioxide.

In all of the planets the radioactive elements uranium, thorium, a form of potassium, and others contained in the rock of their crusts generated heat at a rate considerably higher than at present. This resulted in a great deal of volcanic activity which released large amounts of water previously bound as water of crystallization in the rock. The earth began to acquire her present oceans. The same process should have produced oceans on Mars and Venus, although it is possible that the temperature on Venus was always above the boiling point of water so that the water remained as steam in the atmosphere. By now, however, after several billion years of ultraviolet light from the sun stripping hydrogen atoms out of water molecules in the high atmosphere, both Mars and Venus have lost all of their water. Only on the earth has a fine balance of gravity, temperature, and radiation intensity been maintained to permit the retention of liquid water for four billion years.

During the first billion years on all the planets another process was taking place in their primordial atmospheres. The action of ultraviolet light from the sun in knocking hydrogen atoms out of methane and ammonia molecules which was responsible for the gradual escape of the original atmosphere, left behind what are called "free radicals" of carbon or nitrogen atoms with one or two hydrogens attached. These are very active chemically and react with other constituents of the atmosphere to form a great variety of organic compounds. It is easy to repeat this process in the laboratory today.

In this way, as the earth's oceans slowly grew, rains continually washed into them a rich stock of organic materials out of which living things would in time be made. Another role of the oceans was to dissolve carbon dioxide out of the atmosphere and convert it to solid carbonates like limestone.

In the early years of the young earth, after a billion years or so of chance combinations and accidental associations, by processes not clear at present, the first primitive organisma were formed. We know that his had been accomplished when the earth was only a billion and a half years old. There is a black chert in south central Africa which radioactivity dating shows to be three billion years old. Polished sections of this material reveal by very special and sensitive techniques of electron microscopy the presence of bodies similar to rod-like bacteria fossils trapped in the mud of an ocean bottom three billion years ago and encased in the rock which formed it.

Over millions of years of changing environments, there was a continuous change in the types of organisms making up the populations of living things in the oceans. Thus life developed and evolved as the oceans continued to grow, acquiring more water from spasmodic periods of volcanic activity. Different organisms reproduced and multiplied by feeding on each other, and in this process oxygen was released from the carbon dioxide, and water was continuously fed into the atmosphere from the teeming life in the oceans.

By a billion years ago the original atmosphere was gone, or nearly gone, leaving behind nitrogen, carbon dioxide, and water vapor, with a sizable quantity of oxygen released from the oceans by photosynthesis. As the amount of oxygen built up, a layer of ozone began to form high in the atmosphere. Ozone strongly absorbs ultraviolet light and when it was present in sufficient quantity it shielded the lower atmosphere and oceans from the previously intense ultraviolet radiation which kept all life confined to several feet below the surface of the ocean. The build-up of oxygen in the atmosphere and the formation of the protective ozone layer was preparing the stage for a major change in the history of life on the earth.

The earth was already four billion years old when this major turning point in her long history took place. Shielded from the sun's ultraviolet radiation, a vast elaboration of multi-cellular organisms took place which produced great coral reefs, a profusion of sea animals called "trilobites" and the first fish. In another 300 million years the land had become clothed with vegetation and many insects had evolved. But at that time when the earth was already 4,300 million years old there was not a particle of coal, a drop of oil, or a bubble of gas anywhere in her crust. These great reserves of fossil fuels were laid down over the next hundred million years as though the earth were being stocked with them for some future need. Surely this rare and precious resource was not meant either to be recklessly squandered in a short two or three centuries.

This period was followed beginning 200 million years ago by the age of the great dinosaurs and then beginning 70 million years ago by the age of the mammals. When that age ended just two million years ago the scene had become very familiar. As yet there were no men on the earth, but otherwise all across Europe and Asia, the Americas and Africa there were dense forests and fertile steppes clothing the earth in a blanket of green. Throughout this lush verdure were myriads of animals similar to those today. A remarkable planet, a tiny island in the midst of vast reaches of alien space, had brought forth a magic garden, a teeming wonderland, maintained by a fragile balance of light and heat and gravity. A being like an angel or a demon exploring our portion of the galaxy would react with stunned amazement and delight on reaching such a spot in space, so unlike the myriad of other planets he had visited.

People talk very lightly these days about the prevalence of planets like this earth which could support life over a span of billions of years. When they do so they set attitudes for themselves which prevents their appreciating the earth. There are doubtless manl stars with planetary systems in our galaxy. But it must be equally true that the vast majority of planets end up like Mars or Venus or Jupiter. We do not know all the conditions a planet must satisfy to permit the retention of oceans of liquid water for billions of years while allowing the escape of the primordial atmosphere of ammonia and methane in time for a nitrogen-oxygen atmosphere to replace it so that a full and luxurious development of life can take place on it. But these conditions must be very stringent indeed. Almost certainly there is not another place like the earth within a thousand light years of us. If this be so, the earth with its vistas of breathtaking beauty, its azure seas, beaches, mighty mountains, and soft blankets of forest, and steppes is a veritable wonderland in the universe. It is a gem of rare and magical beauty hung in a trackless space filled with lethal radiations and accompanied on its journey by sister planets which are either viciously hot or dreadfully cold, arid and lifeless chunks of raw rock. Earth is choice, precious and sacred beyond all comparison or measure.

For most of its history the earth had no concentrated bodies of rich ores. Slowly over billions of years two processes working alternately produced them. One is the steady accumulation of radioactive heat deep in the earth's crust erupting from time to time in great mountain-forming upheavals with volcanoes and earthquakes. In between these geologic revolutions, wind and water worked a slow erosion back to flat plains and swamps. Throughout these changes alternating and selective solution and precipitation, melting and recrystalization, concentrated one compound here and another there in the earth's crust. It is necessary to know that the rich bodies of copper and tine, of iron and uranium, of gold and silver, which we so recklessly gouge out of the earth, took a billion or more years to be concentrated and stocked for us. They were surely not meant to be squandered in a single century.

Two million years ago, which is practically now in a 4600 million year history, a new geological epoch called the Pleistocene began. Although it was not evident then, it is now clear that this was the most fateful and decisive moment in the whole long history of the earth. The reason is that the mysterious creative drive in the evolutionary process began then to produce man. The process unfolded in several stages and did not reach our species, Homo sapiens, until just some 40 thousand years ago. Even then his presence did little to alter the pastoral tranquility of the earth until quite recently. It was only 10,000 years ago that man first began to practice agriculture and build permanent villages, and only 5,000 years since the first civilization emerged. But from the moment of his creation the potential was there for a drastic change. This strange new creature would in time fill the earth and subdue it and take dominion over all creatures.

The introduction of man among the manifold species which the earth had, produced a revolution in the earth's history.

The whole planet began to glow under the thought and spirit possessed by this species known as Homo sapiens. Clearly this was a fateful moment for the earth in her immensely long history. The transformation has the potential of becoming a great blessing carrying the planet to new heights of beauty, loveliness, creativity, and spirituality. It has equally the potentiality of becoming a great curse for the earth finally leading to the poisoning and fouling of her atmosphere, the choking to death of her rivers and lakes, the transformation of the wild beauty of her wildernesses into vast dump heaps of refuse, the extinction of most species of living things other than man. Which it is to be, a blessing or a curse, is the central question before man in the last third of the twentieth century.

By the end of this century, it now appears that the earth will be really full of men. But worse, it threatens to be subdued and despoiled by man. All over its surface, will his sprawling cities pollute the landscape? Without limit in every direction, will the fields and factories of man, his highways and bridges and power lines cover the earth? Will all of the rich accumulations of iron, copper, tin and many other metals have been gouged out of the earth and squandered? Will the total supply of oil and gas, so painstakingly accumulated and stored in the earth for man 200 million years ago, already have been drawn out and burned? Will most of the strange and lovely species of animals and birds with which man so recently shared the adventure of life have become extinct? Perhaps, a few will remain in national parks and zoos maintained by man in his nostalgia for a lost paradise. Will the great rivers and lakes of the earth all have been fouled and dead or dying, and the atmosphere above reek with the vast outpouring of offal from the cities and factories of man?

If civilization is really headed in this direction, one can only conclude that it was a cosmic blunder to have allowed man to evolve on the earth. Never before in the long, amazing, and wonderful course of life on this planet had the introduction of a single species proved to be a lethal factor for all other species and indeed for the ecological principle on which the earth up to then had depended for the support of the whole process of life.

There is something wrong in the exercise of man's dominion over the earth if the ultimate effect of his much vaunted technology is to convert the wilderness into a dump heap. We require a massive redirection of our science and technology if we are to avoid disaster. The course of science has been marked by an ever increasing fragmentation into narrower and narrower specialities. Our best scientists concentrate their genius on understanding more and more about less and less, without concern for the overall network of relationships by which nature as a whole hangs together.

For nature is a whole and man is as much a part of nature as stones, and trees, and other mammals. In the exercise of his dominion over the rest of nature then he cannot lift himself out of nature. Man and his planet are inextricably bound together. When he inadvertently applies his scientific skills in ways that upset the balance of nature he is as much a victim of the imbalance as the rest of nature because he is as much a component of nature as everything else. Yet the whole delicate fabric of interwoven relationships and laws which determine the balance of nature are as much an object for scientific investigation and understanding as any of the multiplicity of prestigeous narrow specialities which now consume our best scientific talent. If science is not ultimately to destroy itself, a way must be found to divert increasing numbers of our most talented students into such broad concerns as ecology. This course is a step in that direction.

Man has an inescapable role to play in his exercise of dominion over the rest of nature, and there is no way he can escape this role. Yet, too often, he has used his dominion over nature with arrogance and contempt for everything but himself. In the days of the pioneer in America, Nature was an enemy to be conquered. Strong men, women and children pitted their energy and skill against a wild and fearsome environment. The lives of a man and his family depended upon his ability and determination to conquer a hostile nature of overwhelming power. Nature was and often still is a dark and fearful adversary to all peoples of the world. Hurricanes, typhoons, tidal waves, earthquakes, volcanos and other natural disasters make us realize the awesome destructive power of Nature and the puniness of man. Even so, with the full development of our science and technology and the conversion of the earth into our spaceship, we are beginning to stand aghast at the consequences of man looking upon Nature as an enemy to be conquered. There must be a better way, and there is.

This is to exercise our dominion over the earth by appreciating what a marvelous space ship our planet really is. This means that each individual must care for his little bit of the good earth, with appreciation that borders on love. For example, English gardens and parks, the neat and lush countryside, the graceful groupings of lovely buildings in towns and villages, bespeaks of a relationship between man and the earth which enriches and ennobles both. The same impression is created by a field of hybrid corn in Iowa, a green pasture with a fine herd of cattle in Lancaster County, Pennsylvania, the scrubbed marble steps of modest homes in the east side of Baltimore, Maryland - just to mention a few.

This exercise of loving Nature, this active wooing of the earth, could, if universally practiced with all the resources of modern science and technology, gradually transform our spaceship into an object of grandeur and loveliness of which it could not have been capable without man. For man it would mean the restoration of a life-giving, truly human environment that would nurture and elevate his spirit to new heights of achievement. It would also mean the full development of the potentialities of this good earth. But it cannot be achieved without love.

The present outlook points toward a bleak and disastrous future. To date, somehow or other, man has muddled through wars, pestilences, and natural disasters. The suffering and consequences were localized in that they did not affect the entire earth. The world's present and projected population together with its demands for more and more things and services means that the excesses of civilization will no longer be localized. It therefore seems that there is no hope of a way out of this awful dilemma. Yet there must be.

The salvation of the future for a good life on this earth for all mankind depends upon completely unforeseeable developments. This hope is grounded in the conviction that the long evolutionary process which produced man on this planet and brought him to his present predicament had meaning and purpose. Too much investment has gone into him to have it wiped out completely. Admittedly it will take a miracle to save man, but miracles have happened before and hopefully will happen again. The past history of our species is marked with many miracles which were wholly unforeseen by those involved in them, but constituted major turning points in human development. There is some hope that this constructive drive will continue to mark our future history.

Even with this ultimate hope, however, it seems inevitable that we will suffer much agony in the immediate future. As we are crowded and compressed together in the next few decades, there are bound to be social upheavals of severe intensity - maybe worse that any we have experienced so far. Sooner or later if world wide population explosions continue, there are bound to be catastrophic famines with attendant threats of epidemic disease. All this may well disrupt the established order of many nations and accepted ways of life. This last third of the twentieth century will surely be a time of judgment for man far more severe than any he has ever before experienced. Much that we cherish would then be destroyed never to be recovered again. But then, again, maybe not. Much depends upon those who read these words and are motivated to do something constructive about the problems that face us - before it is too late. There could be no greater motivation for any student looking for a worthwhile career than to prepare himself or herself for losing themselves in such a challenging life's work.

If we fail and civilization as we know it dies, then something new will arise from the ashes as different from our civilization as it differs from that of more than 5,000 years ago. Of course, there is no way to even imagine what that post-civilization will be like. It may be so much better than today's that the suffering we may endure will be worth the price we pay.

But since we still have time to mend our ways, let us remember that the time of judgment is also a time of challenge of great opportunity for those with the courage, the faith, and the hope to live confidently in the midst of great revolutionary change - and to help mold that change into something good and wholesome. The future of both man and his good earth depend on having such people at this critical time. Through them and their efforts the new age will dawn better than the old.

THE PROBLEM

Is There An Answer?

SUMMARY

To date, America has not faced a water crisis primarily because large areas of our country have been blessed with adequate rainfall, lakes and reservoirs to store it, and rivers to distribute it - with the help of tremendous engineering feats. However, normal growth in population and affluence pose definite threats for the not-too-distant future. Even now, many of our major water resources are polluted to the point of real danger. This minicourse attempts to analyze this important problem objectively.

ACKNOWLEDGEMENT

The author appreciates the constructive suggestions made by Dr. Joe Allen of Clemson University.

PREREQUISITES

None.

OBJECTIVES

After studying this minicourse, the student should:

1. Have a better appreciation of the water situation in the United States.
2. Be motivated to want to learn everything possible about this problem.
3. Consider devoting his career to helping solve this problem.
4. Become active in supporting legislation and legislators devoted to solving this problem.
5. Do all in his or her personal life to conserve water and prevent its pollution.
6. Do all in his or her actions to interest others in conserving water and preventing its pollution.

The objective of this [illegible] to present
a minicourse of water chemistry
designed to solve engineering
and pollution problems for the [illegible]
conservationist, the legislator,
the mining engineer, the agricultural
engineer, the forester, the civil
engineer and the municipal
planning engineers <—

I. INTRODUCTION

The United States of America is a great country. So great and so wonderfully blessed that - almost until now - its people could indulge in the foolish luxury of being careless. An isolated farm could dispose of its waste without causing any hazards to itself or others. But the vast and unprecedented growth in population, affluence, and industry poses problems that must be met with sensible haste, scientific skills, and appropriate scope and effectiveness. The view we now see is intolerable.

Exercise 1 Describe fifteen examples of deterioration of our environment with which you, personally, are familiar.

Some examples you may have come up with are:

1. Piling of tailings from coal mines and other mining operations that destroy our green valleys.
2 Unplanned logging of marvelous forests.
3. Wanton and thoughtless destruction of wildlife and marine life.
4. Turning marginal lands into farms with resultant dust bowls and erosion.
5. Gobbling up of good farm lands for the construction of roads and cities.
6 Overpopulation.
7. Depletion of petroleum, coal, and other valuable and irreplaceable mineral resources.
8. Promiscuous use of insecticides and other chemicals.
9. Encroachment on and destruction of tide water salt marshes.
10. Soil erosion.
11. Auto graveyards and other junk heaps.
12. Municipal dumps.

13. Beer cans, bottles, and wastepaper strewing our highways, parks, and waterways.
14. Spent lubricating oils pouring into streams - and everywhere.
15. Pollution of our streams, rivers, lakes and bays by industry.
16. Pollution of our streams, rivers, lakes and bays by inadequately treated domestic wastes.
17. Pollution of our streams, rivers, lakes and bays by farm run-off.
18. Pollution of our streams, rivers, lakes and bays by all types of water craft.
19. Dumping of sewage sludge into the ocean.
20. Air pollution by a multitude of offenders.

The above list is not intended to be complete by any means, but it does indicate the magnitude of the problem that faces civilized man, for he cannot exist without an adequate supply of good, clean, fresh water. This has governed the activities of mankind from Bible days to Singapore, for a city can be seiged and taken without a fight if its water supply can be stopped. Such was the threat to the United States naval base at Quantanamo, Cuba, and it took heroic measures to meet that crisis.

Exercise 2

Do you believe some of these crises are exaggerated? Try to support your opinion on this from news information you have read or heard over the past three to six months.

The drought in New England and the water shed supplying New York City made us realize a few years ago the seriousness of overcrowding in that heavily populated and industrialized part of the country. Such problems are bound to occur more and more frequently in the years ahead unless adequate measures are taken to cope with the complex situation.

It is bad enough to flip a switch and remain in darkness, or be trapped between floors in the elevator of a skyscraper. It will be a problem several magnitudes greater to turn a valve and have no water flow - no water for drinking, no water for food, no water for cleanliness, no water for sanitation, no water for fighting fires, no water to generate steam to heat our homes or run our factories, no water for farms.

These are problems we should never have to face, but we do face them. The United Sates currently consumes about 400 billion gallons of fresh water every day. By 1980, the nation will need 597 billion gallons per day. The supply of fresh water projected for 1980 is 515 billion gallons a day, thus a daily deficit of 82 billion gallons per day is expected within less than ten years. In addition, some of our water is being used over and over again until the quality is severely deteriorated. For example, water from the Colorado River is used so much and so many times that by the time it reaches Mexico it is, at times, unsuitable even for irrigation. The Mexican government may require our help to solve this problem by means of an international treaty.

As will be pointed out later in the course, there are many things that can and almost certainly will be done to meet this crisis. For example, the reuse and/or recycling of water may be a feasible way of solving the problem for some years to come as long as the quality is not allowed to deteriorate. Another effective way will be to charge more for this essential element of life. The mere fact that water has always been so abundant and cheap has blinded us to its real value and our complete dependence upon it.

Exercise 3

Sugar costs around $0.59 per pound, salt about $0.25 per pound, and water costs around $5 per thousand gallons. Compare the cost of water, per pound, to the cost of sugar and salt. Are you willing to "make up the difference"?

II. THE SUPPLY

Exercise 4 Look at a globe or world map. Approximate the percentage of the surface of the earth which is covered by water.

Actually, water covers 71% of the earth's surface; the world possesses 326 cubic miles of water - and that's a lot by any standard of measurement.

However, 97% of the world's supply is ocean water, which means that it is unfit for human consumption because of its salt content. Most of the remaining 3% is inaccessibly frozen in ice caps and glaciers. Lakes, streams, rivers, and underground reservoirs account for only 0.6% of the total supply.

Even this amount is not uniformly available or wholly acceptable in quality. Concentrations of population and/or droughts can upset an area's supply-to-demand ratio - as it did in New York City. Very large parts of the world are arid deserts and wastelands. As for accepted quality, a recent survey of United States municipal water supplies showed that 6,000 communities - their combined population in excess of 40 million - do not meet the recommendations of the Public Health Service. Some 1,150 communities have water supplies exceeding 1,000 ppm of dissolved solids; drinking water standards of the P.H.S. recommend a dissolved solids limit of 500 ppm.

Exercise 5 Does your community meet the above standards? You should be aware of this: how can you find out? What did you find?

Years ago there was a popular song which stated that the best things in life are free: birds that sing, flowers in spring, sunshine and rain, belong to everyone. These are the blessings that we take for granted and until recently we had every right to do so, for water is continuously circulating through the unending hydrologic cycle of precipitation, runoff, infiltration, storage, evaporation and reprecipitation. The source of a water supply merely means that point in the natural cycle where water is temporarily removed to be used for a while and then given back to nature. Man's effect on nature is to deplete the ground water resources by draining from this underground storage without replacing the borrowed water, as is usually done in the case of a surface supply. Man's depletion of ground water supplies has thus become quite serious in many localities. For example, the "infinite" supply of water in the Permian Basin of west Texas was once found at an average depth of 30 feet underground; the water supply is now 300 feet beneath the surface.

Exercise 6

If the supply of good, clean, fresh water is a serious problem in the United States - and it really is - two questions face the nation: (1) who is to blame and (2) what can be done about it?

Believe it or not, the good guys - you and I - are to blame. (For who, in his own opinion, isn't a good guy?) That's the answer in a nutshell but if you don't like nutshells, let's look at it in more detail.

To gain perspective regarding the urgency and seriousness of the pollution problems that face us, we must not allow ourselves to be lured into complacency by saying that mankind has successfully coped with many crises during the past few thousand years. If we are talking about crises, that's one thing, but catastrophes are something else, for there is a tendency, temptation, justification, and danger of viewing a current problem with more alarm than history justifies:

(a) It is believed that an enormous tsunami wave destroyed the entire mediterranean costal regions about 1175 B.C. This might have been the wave that destroyed the Egyptian armies that pursued Moses and his people.

(b) The fall of the Roman Empire was a severe blow to law and order of that day.

(c) The Dark Ages seemed to be a period of decay and futility to those who lived then.

(d) The disintegration of the British Empire must have seemed like the ending of a good world order to the average Englishman.

(e) The war in Vietnam - any war - is just plain hell to the innocent peasant and the average soldier.

Exercise 7 Name several other occurences in history which cause more catastrophes than the present American situation.

The current American scene is not a catastrophe; it is serious and dangerous, but it is not a catastrophe. Campus unrest, riots, arson, drug addiction, high divorce rates and general moral decline can destroy a people if the percentage of wastrels exceed a certain limit, thus undermining the whole. We may or may not be approaching the danger point in this respect; we may or may not be returning to a saner pattern of overall behavior. At their worst, however, these are dangers that must and can be faced and overcome, but they are not yet catastrophes.

The catastrophe of which we speak is the destruction of life on the earth; the wiping out of civilization as we know it. Not by war, or famine, or plague - but by overpopulation and insatiable appetites. Not for America alone, or the North American Continent, but the entire world. May I repeat, you and I are responsible for the catastrophe - if there is one - that may destroy civilization as we know it. It's the good guys, the hard workers, the successful businessman, the creative scientist, and the efficient homemakers who are the real culprits. Furthermore, just as you and I created the possibility of an impending catastrophe, you and I are the only ones who have a chance of preventing it.

Exercise 8 What is it that we have done that is so sinister that it may destroy civilization upon the entire earth's surface? Why is it that only you and I can prevent it? Why?

Because you and I demand or allow:

(1) Air conditioners rather than suffer through a little heat as our grandparents did.
(2) A multitude of cars for going to and from work rather than using public transportation.
(3) Automatic dish-washers and clothes washers that consume huge amounts of precious water.
(4) Non-returnable bottles, cans, and cartons

that clog our waste disposal systems.
(5) Huge amounts of newspapers, paper towels, and hundreds of other items that further add to our solid waste disposal problems.
(6) Air pollution.
(7) Noise - jets, trucks, T.V., radio.
(8) Population explosion.
(9) Destruction of wet-lands, marshes, and other natural resources. (Pardon the repetition but it is justified.)
(10) Industrial pollution.

Perhaps in self-defense, I honestly don't think that you and I set out to be so sinister. We thought it was wonderful to let the genius of man discover new things, grow more food, produce more cars, build more roads, have modern conveniences in our homes, fly faster - and pour our waste down the drain. If we thought about it at all, we took for granted that the earth could absorb the sewage, the ocean was big enough to dispose of the garbage, and the atmosphere vast enough to take care of the smoke and waste gases. Maybe they used to be, but now they are not.

There have been times when I was struck with the beauty of the earth, but I'm afraid I didn't realize how truly unique and wonderful it really is. There has never been any doubt in my mind that all this didn't just happen, but I had no idea that it took 4.6 billion years to do it.

There is considerable doubt as to whether or not you, I, and the rest of us will be wise enough, soon enough, and in sufficient number, to make the sacrifices to comfort, luxury and family size that must be made in order to avoid the impending catastrophe. The youth of today must face up to these problems in a very few years. I hope they will have the courage, wisdom and spirit to make this a better Earth because they have lived on it.

Human nature being what it is, few individuals will voluntarily offer to forego their accustomed comforts. Therefore it will be the patriotic duty of the average citizen to elect officals who will legislate those drastic measures which will guarantee that all of us make these sacrifices as well as utilize the resources of modern science for the active wooing of the earth. This we will do even though it means increased taxes and decreased privileges. So, whether or not the impending catastrophe actually occurs does depend on you and me.

Exercise 9 Again, do you believe this to be too pessimistic a view? Why, or why not?

III. STEPS TOWARD SOLUTIONS

THE FEDERAL WATER POLLUTION CONTROL ACT OF 1972

Now to answer the second question - what can be done about it.

The following are excerps from the "Federal Water Pollution Control Act of 1972." All students who are interested in this field should be required to read this Act and keep up-to-date on Federal and State laws that affect the nation as a whole and their locale in particular.

"The objective of this Act is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters. To achieve this objective:

(1) the discharge of pollutants into the navigable water are to be eliminated by 1985.
(2) wherever attainable, an interim goal of water quality which provides for the protection and propagation of fish, shellfish, and wildlife.
(3) the discharge of toxic pollutants in toxic amounts be prohibited.
(4) Federal financial assistance be provided to construct publicly-owned waste treatment works.
(5) areawide waste treatment management-planning processes be developed and implemented to assure adequate control of sources of pollutants in each state.
(6) a major research and demonstration effort be made to develop technology necessary to eliminate the discharge of pollutants into the navigable waters, waters of the contiguous zone, and the oceans."

"The Administrator of the Act is authorized to make joint investigations with other Federal agencies regarding the condition of any waters in any State or States, and of the discharge of any sewage, industrial wastes, or substances which may adversely affect such waters."

"In the survey or planning of any reservoir by any Federal agency, consideration shall be given to inclusion of storage or regulation of stream-flow, except that any such storage and water releases shall not be provided as a substitute for adequate treatment or other methods of controlling waste at the source."

"The Administrator of the Act shall encourage cooperative activities by the States for the prevention, reduction, and elimination of pollution, encourage the enactment of improved and, so far as practical, uniform State laws relating to the prevention, reduction, and elimination of pollution; and encourage compacts between States for the prevention and control of pollution".

"The Administrator of the Act shall initiate and promote the coordination and acceleration of research designed to develop the most effective practicable tools and techniques for measuring the social and economic costs and benefits of activities which are subject to regulation under this Act. He shall develop effective and practical processes, methods, and prototype devices for the prevention, reduction, and elimination of pollution."

"The Administrator shall establish, equip, and maintain field laboratory and research facilities, including, but not limited to, one to be located in the northeastern area of the United States, one in the Middle Atlantic area, one in the southeastern area, one in the middle western area, one in the southwestern area, one in the mid-west, and one in the State of Alaska, for the conduct of research, investigations, experiments, field demonstrations and studies, and training relating to the prevention, reduction and elimination of pollution. Insofar as practicable, each such facility shall be located near institutions of higher learning in which graduate training in such research shall be carried out."

"The Administrator shall conduct research and technical development work, and make studies, with respect to the quality of the waters of the Great Lakes, including an analysis of the present and projected future water quality of the Great Lakes under varying conditions of waste treatment and disposal, an evaluation of the water quality needs of those to be served by such waters, an evaluation of municipal, industrial, and vessel waste treatment and disposal practices with respect to such waters, and a study of alternate means of solving pollution problems (including additional waste treatment measures) with respect to such waters."

"For the purpose of providing an adequate supply of trained personnel to operate and maintain existing and future treatment works and related activities, and for the purpose of enhancing substantially the proficiency of those engaged in such activities, the Administrator shall finance pilot programs, in cooperation with State and interstate agencies, municipalities, educational institutions, and other organizations and individuals, of manpower development and training and retaining of persons in, or entering into, the field of operation and maintenance of treatment works and related activities. Such programs and any funds expended for such a program shall supplement, not supplant, other manpower and training programs and funds available for the purposes of this paragraph."

"The Administrator is authorized to establish and maintain research fellowships in the Environmental Protection Agency with such stipends and allowances, including traveling and subsistence expenses, as he may deem necessary to procure the assistances of the most promising research fellows----."

"The Administrator, in cooperation with the department in which the Coast Guard is operating shall engage in such research, studies, experiments, and demonstration as he deems appropriate, relative to the removal of oil from any waters and to the prevention, control, and elimination of oil and hazardous substances pollution."

"The Secretary of the Department in which the Coast Guard is operating shall engage in such research, studies, experiments, and demonstrations as he deems appropriate relative to equipment which is to be installed on board a vessel and is designed to receive, retain, treat, or discharge human body wastes and the wastes from toilets and other receptacles intended to receive or retain body wastes with particular emphasis on equipment to be installed on small recreational vessels."

"The Administrator shall, after consultation with appropriate local, State, and Federal agencies, public and private organizations, and interested individuals, as soon as practicable but not later than January 1, 1973, develop and issue to the States for the purpose of carrying out this Act the latest scientific knowledge available in indicating the kind and extent of effects on health and welfare which may be expected from the presence of pesticides in the water in varying quantities. He shall revise and add to such information whenever necessary to reflect developing scientific knowledge."

"The Administrator is authorized to (1) conduct in the Environment Protection Agency, (2) make grants to persons, and (3) enter into contracts with persons, for research and demonstration projects for prevention of pollution of any waters by industry including, but not limited to, the prevention, reduction, and elimination of the discharge of pollutants. No grant shall be made for any project under this subsection unless the Administrator determines that such project will develop or demonstrate a new or improved method of treating industrial wastes or otherwise prevent pollution by industry, which method shall have industrywide application."

"The Administrator is authorized, in consultation with other interested Federal agencies, to make grants for demonstration projects with respect to new and improved methods of preventing, reducing, storing, collecting, treating, or otherwise eliminating pollution from sewage in rural and other areas where collection of sewage is conventional, uneconomical, or otherwise infeasible, or where soil conditions or other factors preclude the use of septic tanks and drainage field systems."

"The Administrator in cooperation with the Appalachian Regional Commission and other Federal agencies is authorized to conduct, to make grants for, or to contract for, projects to demonstrate comprehensive approaches to the elimination or control of acid or other mine water pollution resulting from active or abandoned mining operations and other environmental pollution affecting water quality within all parts of a watershed or river basin, including siltation from surface mining. Such projects are to restore affected lands to usefulness for forestry, agriculture, recreation, or other beneficial purposes."

"The Administrator is authorized to make grants to or contracts with institutions of higher education, or combinations of such institutions, to assist them in planning, developing, strengthening, improving, or carrying out programs or projects for the preparation of undergraduate students to enter an occupation which involves the design, operation, and maintenance of treatment works, and other facilities whose purpose is water quality control."

"It is the purpose of Title II of this Act to provide GRANTS FOR CONSTRUCTION OF TREATMENT WORKS and to assist the development and implementation of waste treatment management plans and practices which will achieve the goals of this Act. The amount of any grant for treatment works made under this Act from funds authorized for any fiscal years beginning after June 30, 1971, shall be 75 per centum of the cost of construction thereof (as approved by the Administrator)."

Exercise 10

Select the six points in this document which - in your opinion - are the most important ones for solving our problem.

The estimated construction cost of sewage treatment facilities for the period fiscal year 1972-74 is as follows:

(In millions of dollars)

Alabama	52.6	Indiana	490.2
Alaska	32.8	Iowa	168.3
Arizona	19.6	Kansas	54.5
Arkansas	51.5	Kentucky	96.1
California	1,429.7	Louisiana	137.3
Colorado	46.1	Maine	140.9
Connecticut	244.8	Maryland	620.1
Delaware	95.6	Massachusetts	547.2
District of Columbia	103.6	Michigan	
Florida	528.1	Minnesota	295.9
Georgia	141.7	Mississippi	57.3
Hawaii	48.1	Missouri	241.1
Idaho	31.7	Nebraska	54.0
Illinois	910.0	Nevada	41.9
New Hampshire	121.0	Oregon	123.7
New Jersey	1,121.9	Pennsylvania	789.5
New Mexico	30.7	Rhode Island	71.2
New York	1,610.3	South Carolina	94.0
North Carolina	134.4	South Dakota	13.8
North Dakota	6.8	Tennessee	169.0
Ohio	840.8	Texas	403.3
Oklahoma	67.1	Utah	20.5

Students are again urged to read all of this Act and to keep current with Federal, State and local laws regarding the protection of the environment. The Act is indeed far reaching in its aims and objectives; only a small part has been quoted above and these quotes have been selected because of their emphasis on education, research and local impact.

It would seem, therefore, that the seriousness of the water pollution is appreciated by the

Congress of the United States and that the actions planned and forthcoming should make a major impact upon the question: 'Is There An Answer'. Now the proof of the pudding will be to put these plans into effective action and to enact further legislation if and when needed.

WATER - ITS CHEMICAL NATURE

SUMMARY

This short course on Water - Its Chemical Nature is so designed that you should be able to follow the logic and the mathematical calculations with the aid of a series of questions. The answers to these questions are written at the end of this study guide. When you feel you understand the information being considered, proceed. At the beginning of this short course, you will be given a brief examination. Use this examination to check your grasp of the information to be covered.

ACKNOWLEDGEMENT

The author is particularly indebted to his friend and colleague - Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College - for converting his original manuscript into the following format.

READING LIST

Hickman, K., I. White, and E. Stark, "A Distilling System for Purer Water", Science, 180, p. 15 (1973).

PREREQUISITES

Before beginning this mini-course, you should be able to:

1. Read chemical formulas and chemical equations.
2. Define: Calorie
   mole
   ion
3. Determine the molecular weight of a substance, using the formula and a periodic chart.
4. Define a covalent and an electrovalent bond.
5. Define osmosis and osmotic pressures.

OBJECTIVES

At the completion of this mini-course, you should be able to:

1. Read a table of ppm and convert to lbs/cubic mile and to % by weight.
2. Define or discuss: Solar evaporation
   Freezing
   Distillation
   Reverse Osmosis
   Ion Exchange
   with reference to purification of water.
3. Identify or describe the conditions which would make each of the above (obj. 2) useful is a given area of the world.

4. Define hydrogen bonding and describe the effect of H-bonding upon the physical and chemical properties of water.

5. Given a list of values of H, rank them in terms of

   (a) most to least exothermic
   (b) most to least stable

6. Calculate the energy involved in changing ice from $0^{o}C$ to steam at $100^{o}C$ (or vice versa) or to any intermediate temperature.

7. State or recognize ways in which the heat of fusion, heat of vaporization, and specific heat of water are used by people.

8. State that water ionizes slightly, giving $[H^+] = [OH^-] = 1x10^{-7}$ mole per liter.

9. Give 3 reasons why water is closer to being a "universal" solvent than any other liquid.

PRETEST

1. We have a water sample which contains 18 ppm Na. This means we have 18 g. in what weight of water?

2. We are quickly running out of lead (Pb.). Using Table II would you expect it to be feasible to extract lead from the ocean? What about iodine? Explain your answers.

3. Discuss two possible procedures for removing elements from sea water.

4. Use the periodic chart to calculate the molecular weight of $CaCl_2$.

5. How many calories would be needed to raise the temperature of 20g. of water at 60° to 80°C?

6. How many calories would be needed to melt 5 pounds of ice at 0°C? 1 lb = 454 g.

7. How many calories would be needed to change 1 lb of ice at 0°C. to steam at 100°C?

8. The unusually large boiling point of water is due to:

   a) its low molecular weight
   b) its low density
   c) the strong covalent bonding
   d) the hydrogen bonding
   e) the strong electrovalent bonds

   Choose the correct answer. (Only one answer is correct).

9. Of the following group of elements, the one group that forms hydrogen bonds is:

   a) F,O,N b) O,S,Se c) C,N,O d) F,Cl,Br e) N,P,As

10. Sea-water contains 0.01 ppm of Iron. The amount of Iron present in lbs. per cubic mile is:

    a) 91.5×10^8
    b) 91.5×10^9
    c) 91.5×10^3
    d) 91.5×10^5
    e) none of these

    Choose the correct answer. (Only one answer is correct).

Exercise 1

What is the most important chemical in the world?

Make no mistake about it, water is a chemical and chemical reactions occur in aqueous media, including our own metabolism which is a series of very many complex chemical reactions. Said differently, man must have an adequate supply of relatively pure water in order to live.

Thus, much time and space has been devoted to the consideration of sea-water since its use certainly will become increasingly critical to the ongoing of an affluent and growing civilization, both as a source of fresh water and minerals.

Since sea-water is unfit for human consumption and most industrial uses, mankind has to depend almost entirely upon rain for its water and rivers that collect and distribute our normally generous rainfall. Our supply of good water has been so bountiful in relationship to our needs that Americans have indulged in the luxury of being wasteful with it. Only recently have we begun to worry about our supply of good water. Our concern is long overdue.

Exercise 2

For that matter, what is water?

Exercise 3

a. If hydrogen has an atomic weight of 1 and oxygen has an atomic weight of 16, this would mean that water would have a molecular weight of __________.

b. What is the molecular weight of CH_4? of H_2S?

It has been observed that, within resonable limits, low molecular weight compounds are more volatile than heavier ones. In other words, low molecular weight compounds are gases, medium weight are liquids, and high molecular weight compounds are solids. For example, methane (CH_4) - ordinary marsh gas - has a molecular weight of 16, almost the same as water (M. wt, 18). Yet water boils at 100°C, and methane boils at -161°C. Then there is hydrogen sulphide (H_2S) with a molecular weight of 34, almost twice that of water, yet it is a gas that boils at -62°C. From such evidence and much more, it is concluded that water is not a single molecule of H_2O, but is a cluster of at least several molecules joined firmly together; these clusters, in turn, are bound to one another due to the attractions of the hydrogen atoms on one water molecule for oxygen atoms on other molecules of water. This is known as hydrogen bonding, about which more will be said later.

The data in the following table substantiates the relationship between molecular weight and boiling point. It is obvious that organic compounds exist in a somewhat different world than inorganic compounds, but the trend is the same. It should also be noted that H_2S, even though it is a gas, has a boiling point higher than would be expected. This is due to its similarity to water, for oxygen and sulphur are next to one another in the periodic system.

TABLE I

Compounds	Formula	Molecular Weight	Boiling Point, °C
Methane	CH_4	16	-161
Ethane	C_2H_6	30	- 88
Propane	C_3H_8	44	- 42
Butane	C_4H_{10}	58	0
Pentane	C_5H_{12}	72	36
Hexane	C_6H_{14}	86	69
Heptane	C_7H_{16}	100	98
Nitrogen	N_2	28	-196
Carbon Monoxide	CO	28	-190
Oxygen	O_2	32	-183
Hydrogen Sulphide	H_2S	34	- 62
Carbon Dioxide	CO_2	44	- 78
Chlorine	Cl_2	71	- 34
Bromine	Br_2	160	59

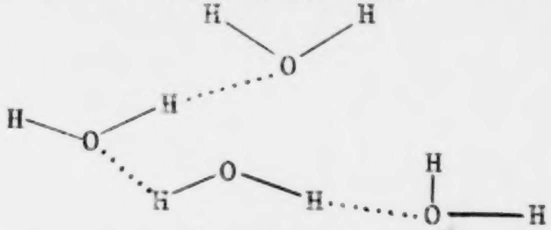
Exercise 4

From this table, what relationships do you see between the boiling points and molecular weights of these compounds?

Let us consider in particular the hydrides of elements in Group VI Viz., H_2O, H_2S, H_2Se, H_2Te. We would expect on the basis of the general trends observed in Table I, water to have the lowest boiling point.

Boiling Point
H_2O : 100°C
H_2S : - 85.6°C
H_2Se : - 60.4°C
H_2Te : - 51°C

W. M. Latimer and W. H. Rodebush suggested that the molecules of water are strongly attracted to each other (associated) in the liquid phase giving the effect of high molecular weight. This intermolecular association occurs through a "hydrogen bond" (shown as ----) in three dimensions:



Ordinary ice contains a high degree of hydrogen bonding, which accounts for its high rigidity. In ice each water molecule is attached tetrahedrally to four other water molecules by four hydrogen bonds. No other element besides hydrogen exhibits this type of bonding, because hydrogen is the only atom whose nucleus is not shielded by electrons in the inner shell. Hydrogen bonding is present only in those compounds, where the hydrogen atom is covalently bonded to elements having great affinity for electrons, namely F, O and N. Other examples of hydrogen bonded compounds are:

a) HF - Hydrogen fluoride in liquid phase
b) CH_3COOH - Acetic acid in vapor phase
c) Proteins

Hydrogen bonds are weak bonds and require only 5 to 10 Kcal/mole to be broken, whereas 50 to 100 Kcal/mole are required to break a covalent bond.

Additional evidence regarding the unusual nature of water is its high heat of formation. Some students may have covered this ground in an earlier course; to others it may be a new concept requiring some extra study. Even so, it should be fairly obvious that the energy required to pull apart a chemical compound is a measure of its stability or the strength of the bonds holding it together. It should be equally obvious, then, that the reverse has to be true: the amount of energy released when a compound is formed or put together - measures the stability of the compound. A comparison can also be made between the heats of combustion. More energy is released per gram when hydrogen burns with oxygen to form water than with the combustion of any other fuel. In other words, this is proof that water is an extremely stable compound. This is the reason that the satellites were powered by the reaction:

$H_2 + 1/2\ O_2 \rightarrow H_2O$ ΔH = -34,000 calories per gram of H_2 burned.

For purpose of comparison, the energy released per gram of some fuels are:

Fuel	Heats of Combustion ΔH @ 25°C., in cal/gram
H_2	-34,000
C	- 7,830
CH_4	-11,800
C_3H_8	-12,000
C_2H_2	-11,900
C_6H_6	-10,000

In all cases the above figures are based on burning the various fuels to liquid H_2O and gaseous CO_2. The minus sign means that energy has been released by the burning of the fuel with O_2; a plus sign indicates that energy has been absorbed.

Exercise 5

Rank each of the following hypothetical reactions, with the most exothermic reaction first:

(a) $A + 1/2\ O_2 = AO$ $\Delta H = -7{,}000$ cal/g.
(b) $B + 1/2\ O_2 = BO$ $\Delta H = -15{,}200$ cal/g.
(c) $CO = C + 1/2\ O_2$ $\Delta H = +8{,}400$ cal/g.

Other unique properties of water - and very practical ones - are its:

a) High heat of fusion. It requires the removal of 80 calories to convert one gram of water at 0°C to ice at the same temperature. This is an excellent source of refrigeration.

Exercise 6

How much heat would be required to convert 50 grams of water at 0°C to ice at 0°C?

b) High heat of vaporization. It requires 540 calories to change one gram of water at 100°C to steam at the same temperature. Consequently steam is used as a means of transferring heat from one place to another.

Exercise 7

If 50 grams of water at 100°C were vaporized at 100°C, how much energy would be absorbed?

Substances differ in the amount of energy required to raise their temperature. Each has its own value, which we call specific heat. The specific heat for a substance is the quantity of energy required to raise the temperature of 1 gram by one degree centigrade.

Example: The specific heat of water is 1 calorie/g. degree.

Exercise 8

What amount of energy is required to raise the temperature of 50 g. of water by 8°C?

Exercise 9

Calculate the number of calories required to melt 50 grams of ice at 0°C and convert the resulting water steam to 100°C.

a. What is the amount of heat needed to melt the ice?

b. What is the amount of heat needed to raise the temperature of 50 g. of water from 0°C to 100°C?

c. What is the amount of heat needed to vaporize the 50 g. of water at 30°C to steam at 100°C?

d. What is the total amount of heat needed to convert 50 g. of ice at 0°C to steam at 100°C?

One can readily understand why steam at 100°C is more dangerous than water at 100°C - it contains 540 additional calories per gram.

Now you try a problem by yourself.

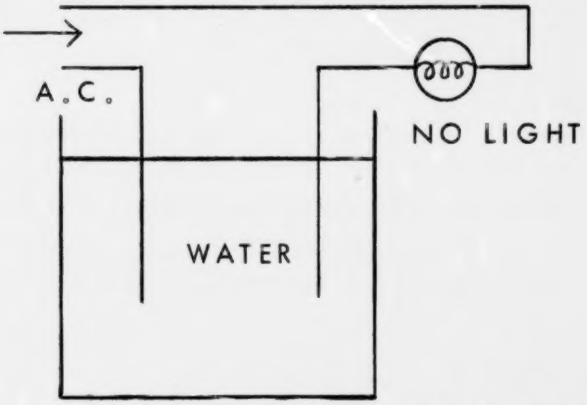
Exercise 10

How many calories must be removed to change 8 grams of steam at 100°C to ice at 0°C.?

c) Electrical conductivity

In discussing any particular phenomenon of chemistry, teachers are often guilty of being carried away with the importance of the subject at hand thus stating that it is the most important thing in the world. One is tempted to make such a statement regarding the next unusual property of water that we will now consider. It so happens that water isn't entirely H_2O; it is almost, but that small bit that isn't H_2O makes a tremendous difference in its properties and behavior.

If two wires or electrodes are dipped into a beaker of pure water and connected externally to an electric light bulb and a battery hooked in series - in the manner shown in Figure 1 - it would be noted that the bulb does not glow. This indicates that there is no flow of electricity; that is, pure water does not conduct electricity.



If, however, our testing device were sufficiently sensitive, we would discover that an extremely small amount of electricity does flow even with the purest of water. (More will be said about this when electrochemistry is covered later in the course). For the present, it is sufficient to know that ions must be present in water for it to conduct electricity. Since a very small amount of electricity flows, there must be very few ions present in pure water. There are, and this is the equation that tells the story:

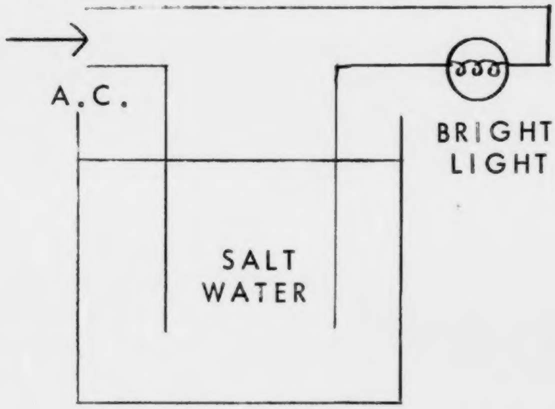
$$H_2O \rightarrow H^+ + OH^-$$

Careful measurements show that the concentration of H^+ (usually written as H^+ are 10^{-7} moles per liter. Said differently, there are one-ten millionth moles of hydrogen ions in a liter of water. Since pure water is neutral, the OH^- concentration is also 10^{-7} moles per liter. This is expressed as:

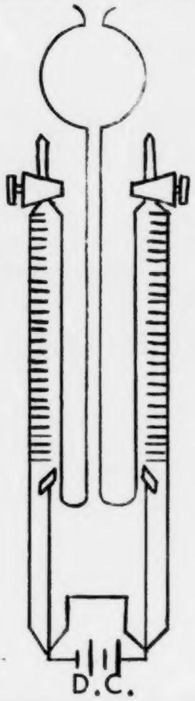
$$K_w = [H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

K_w is the ion-product constant of water and equals 10^{-14} at room temperature. (It changes - increases - somewhat at higher temperatures). It states mathematically a most important property of water: no matter what is done to water, $K_w = 10^{-14}$.

To unravel all the secrets of water has not been an easy task, but the few examples cited above have led chemists to recognize that the extremely unique properties of water - and particularly the fact that it ionizes ever so slightly - somehow enables it to dissolve a great number of substances. Furthermore, many of these solutes - usually salts - form large concentrations of ions in water which are capable of conducting electricity very well.



If direct current is passed through water to which a small amount of H_2SO_4 has been added to increase the conductivity, as shown in Figure 2, bubbles of gas would collect on and be liberated at each electrode. It would be instructive to collect these gases in some such fashion as:



It will be found that more gas collects in one tube than the other in the ratio of small whole numbers. Also, these gases are quite different and the amount of gas formed is proportional to the amount of elecricity used. These are precise quantitative relationships that will be developed more fully later on.

Exercise 11

If Figure 2 were used for the electrolysis of H_2O, which of the tubes shown would represent formation of H_2O? Which O_2? How do you know?

Water comes closer to being a universal solvent than any other liquid. Introductory college chemistry usually sets down a set of rules regarding the solubilities of compounds in water and in general these say, "all this and that are soluble in water, except....". The more one studies chemistry the more these exceptions must be studied and understood in detail. But it is true that even those chemical compounds we classify as insoluble are slightly soluble and the chemistry of these are so important that a separate mini-course will be devoted to them.

Exercise 12

We are surrounded by vast oceans - three-quarters of the earth's surface is covered by water to an average depth of about two miles. It would then seem that America's large coastal cities would have plenty of water for their domestic and industrial needs. Is this true or false? Explain your answer.

Sea-water contains large quantities of dissolved salts. Actually, almost everything imaginable is found in sea-water: leading the list is sodium chloride at 2.67%. This amounts to 10,500 ppm of Na.

Exercise 13

What is the meaning of parts per million?

Exercise 14

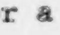
a. What is the formula for sodium chloride?

b. This means that one mole of Na requires how many moles of Cl to make a mole of the salt? NOTE: In this case, a mole is one gram atomic weight.

c. Refer to the periodic chart or a table of atomic weights. The atomic weight of Na is __________ and that of Cl is __________.

d. The ratio of the atomic weight of Cl to Na is __________.

Exercise 15

What is the meaning of the symbol  ?

We know that the chloride in sodium chloride is 1.5 times as heavy as is the sodium, or in the same volume of sea-water the weight concentration of chloride is 1.5 times the concentration of sodium.

Exercise 16

If, as in our problem, sodium has a concentration of 10,500 ppm, then calculate the chloride concentration.

Exercise 17

The concentration of sodium chloride (NaCl) would be equal to the concentration of Na, __________ppm, plus the concentration of Cl, __________ppm, or a total of __________ppm of NaCl.

Exercise 18

With the above exercises as a foundation, show that 2.67% NaCl = 10,500 ppm NaCl.

The wide oceans of the world contain a constant content of total salts, 3.5%. Thus, something slightly less than 1.0% of the total weight accounts for all other salts in the ocean.

Exercise 19

Explain how we obtain the 1.0%.

These are a veritable store house of potential wealth that certainly will be tapped in the not-too-distant future. Even now, magnesium and bromine are being profitably extracted from sea-water; for example, there are six million tons of magnesium in one cubic-mile of sea-water.

Exercise 20

a. You know that 5280 ft = 1 mile, then calculate the number of cubic feet in 1 cubic mile.

b. We should write the problem in the scientific form of $(5.280 \times 10^3)^3$ cu. ft. = 1 cu. mi. which becomes __________ cu. ft. = 1 cu. mi.

c. We also know that 1 cu. ft. of water weighs 62.4 lbs. Calculate the weight in lbs. of 1 cu. mi. of water.

The following table shows that sea-water contains 1350 ppm of Mg which may be written as: $\frac{1350 \text{ lbs Mg}}{1 \times 10^6 \text{ lbs } H_2O}$.

Exercise 21

If we have one cubic mile of water we would have:

a. How many lbs. of Mg?

b. How many tons of Mg?

In like manner the following tables were calculated for the other elements contained in a cubic mile of sea-water.

Many critical minerals such as Cu, Pb, Zn, Sn - just to mention a few - are being consumed at such a rate that the world's supply may well be exhausted by the turn of the century. As can be seen from the following table, the oceans contain an inexhaustible quantity of every inorganic element needed by man. An attempt has been made to calculate the value of a few which may have a chance of competing with land based sources. The overall dollar value is attractive, but the concentrations of most of the ions are so slight that it now appears impractical to try to extract most of them using known procedures - the cost of handling huge amounts of sea-water would be greater than the materials removed - even if they could be.

If and when the need exceeds the supply, the economic picture will change accordingly and drastically. Many new techniques potentially applicable to the handling of large volumes of dilute liquids have been proposed during the past decade or so, and it is likely that these and others will enter the picture either singly or in series.

As things now stand, one authority (1) believes that chlorine, sodium, magnesium, potassium and bromine can be economically recovered from sea-water at costs competitive with land based sources. As stated above, magnesium and bromine are already being extracted commercially from sea-water. It would seem to me that it will be a long time before the recovery of chlorine, sodium and potassium can compete costwise with naturally occurring solid sources. However, local needs and new techniques may reverse any current prognostication.

For example, another authority (2) states that in the long term it may well be economically feasible to extract Mo, U, Ag, Au, Sn, Ni, Cu and Co from the waters of the ocean. Certainly the indicated value of the minerals contained in a cubic mile of sea-water sets a lucrative goal for research, and much creative and valuable work is being done in this most challenging field.

As is so often the case with technical progress, one development augments another. For example, man's need for potable water may, as an extremely valuable by-product, enhance the economic extraction of minerals from the ocean. There have been and are numerous attempts to utilize sea-water for human consumption and/or industrial uses.

TABLE II

Element	ppm	Lbs. per cubic mile	Dollars per cubic mile
He	$5x10^{-6}$	45.5	
Li	.17	$1.55x10^{6}$	
B	4.6	$42.0x10^{6}$	
F	1.3	$12.0x10^{6}$	
Ne	$1x10^{-4}$	910	
Mg	1350	$12.5x10^{9}$	2 billion
Al	.01	$91.5x10^{3}$	75,000
P	.07	$640x10^{3}$	
S	885	$8.1x10^{9}$	
A	.6	$5.5x10^{6}$	
K	380	$3.5x10^{9}$	
Ca	400	$3.7x10^{9}$	
V	.002	$18.3x10^{3}$	
Cr	$5x10^{-5}$	455	
Mn	.002	$18.3x10^{3}$	9,000
Fe	.01	$91.5x10^{3}$	
Co	$1x10^{-4}$	910	
Ni	.002	$18.3x10^{3}$	23,000
Cu	.003	$27.5x10^{3}$	40,000
Zn	.01	$91.5x10^{3}$	25,000
As	.003	$27.5x10^{3}$	
Br	65	$600x10^{6}$	100 million
Kr	$3x10^{-4}$	2730	
Sr	8.0	$73x10^{6}$	23 million
Nb	$1x10^{-5}$	91	
Mo	.01	$91.5x10^{3}$	200,000
Ag	$4x10^{-5}$	365	
Cd	$1.1x10^{-4}$	1000	
Sn	$8x10^{-4}$	7280	
Sb	$5x10^{-4}$	4550	
I	.06	$550x10^{3}$	
Ba	.03	$275x10^{3}$	15,000
W	$1x10^{-4}$	910	
Au	$4x10^{-6}$	36.5	20,000

TABLE II (con.)

Element	ppm	Lbs. per cubic mile	Dollars per cubic mile
Hg	$3x10^{-5}$	275	
Pb	$3x10^{-5}$	275	
Bi	$2x10^{-5}$	180	
U	.003	$27.5x10^{3}$	

Exercise 22

What do you see as some of the problems associated with mining the seas? Do you see these as exciting challenges or as a problem to be avoided?

Exercise 23

See if you can use your prior knowledge to briefly explain the following possible procedures for water purification.

1. Solar evaporation:
2. Freezing:
3. Distillation:
4. Reverse Osmosis:
5. Ion Exchange:

Solar evaporation: This procedure has been tried in places such as the shore areas and small islands of the Mediterranean Sea where there is a hot climate and thus plenty of sun, no other source of fresh water, and not too great a demand for large quantities of potable water.

Basically, the procedure is quite simple. Sea-water is pumped into a large basin lined with a black plastic material that holds the water and absorbs the sun's heat. The water vapor -

or distillate - condenses on a transparent plastic cover that forms a dome over the basin in such a manner that the water trickles down the sides into a collecting trough. The sea-water remaining in the basin is thus concentrated and the amount of ion content correspondingly increased. In practice, this process yields so little water that very few places can use it.

Freezing: To understand this, the student should know something about fractional crystallization. Even so, it probably isn't amiss to review the principle briefly. If several substances are dissolved in a liquid - such as water - and the solution is gradually and carefully cooled, crystals will usually form and thus can be removed from the liquid phase (or mother liquor) by settling, filtering, or centrifuging. Thus, dissolved substances can be removed from the liquid with the dual result that: a) the solids are removed from the liquid and b) the liquid is taken from the solids - thus benefiting both phases.

In cold countries like Sweden and Russia, refrigeration is free - to say the least - and thus it is economical to freeze sea-water. As the temperature of the water is lowered, crystals form - crystals of almost pure water - leaving a liquid phase richer in dissolved salts. The purified ice crystals are removed and are a source of potable water. The liquid phase, or brine, or bittern as the English call it, thus contains as much as three times the concentration of dissolved salts as the ocean's water. The economics of recovering these substances from such a brine is thus enhanced by a factor of three.

Distillation: Just as some countries have free refrigeration, others have "waste" heat. At least one Middle East country has so much natural gas and so little fresh water that they are distilling sea-water and delivering it in tank trucks to their thirsty citizens. There are few places in the world that can afford such an expensive procedure, but who knows what will happen when man's thirst for pure water reaches the point of desperation.

Here again, the salt content in the still pot is enriched in solids content, thus making the residue more attractive as a source of many raw materials of great potential value.

Reverse Osmosis: Everyone is a living example of osmosis. The food we eat is broken down by our digestive system into smaller and smaller molecules. When these reach the right size and shape, they pass through membranes and are carried by the blood to the various parts of our body. The spent molecules are next removed from the blood by osmosis, all of which makes us one of the most efficient machines known for converting energy into work - whether or not the work is useful is another matter.

The force driving a molecule through the membrane is known as osmotic pressure and this requires that the molecules go from a high to a lower concentration in the process.

As the term clearly states, reverse osmosis means that dissolved substances are forced - by applied pressure - to go from low to higher concentrations. The DuPont Company has produced a hollow nylon fiber which is thinner than a human hair. Furthermore the synthetic fiber has built into it tiny holes that are large enough to permit the passage of water molecules - under high pressure - but so small that the passage of dissolved salts and other larger molecules is impeded.

Reverse osmosis is being used in a number of commercial applications for concentrating dissolved substances, thus making their recovery economically feasible. One example is the concentration of the dissolved food values in milk whey.

Active research is under way to apply reverse osmosis to the desalination of sea-water because of the favorable energy requirements.

Reverse osmosis is also being studied as a practical and economical tertiary treatment for sewage plant effluents. More will be said about this later on.

Ion Exchange: Zeolite and synthetic ion exchange resins have been and are being used widely for the removal of hardness ions from water in many rural areas. Perhaps no other method is as satisfactory on a small scale as this and a mini-course will be devoted to this subject.

The refinement and specificity of new ion exchange resins, constantly opens up new opportunities for the selective removal of one ion from another in aqueous media - for example, sea-water. The probability of success in this field is obviously enhanced by the enrichment of the solutes by one or more of the above processes.

ANSWERS

A. PRETEST

1) 1 million (10^6) grams.
2) Since iodine is present in a relatively high concentration when compared to lead, it would be far more likely that we can extract Iodine.
3) Refer to pages 38, 39 and 40.
4) 111 5) 400 cals. 6) 181,000 cals.
7) 122,580 cals. 8) d 9) a 10) c

B. STUDY GUIDE

Exercise 1 - water

Exercise 2 - We have already stated that water is a chemical. The chemist says that water is H_2O. That is, it is composed of two atoms of hydrogen combined with one atom of oxygen.

Exercise 3 - a. $12 + 4 = 16$

b. $2 + 32 = 34$

Exercise 4 - As the molecular weight increases, the boiling point also increases.

Exercise 5 - b a c

Exercise 6 - $50 \text{ grams} \times \frac{80 \text{ cal}}{1 \text{ gram}} = 4000$ calories.

Exercise 7 - $\frac{50\text{g} \times 540\text{cal.}}{1 \text{ gram water}} = 27{,}000$ calories or 2.7×10^4 calories.

Exercise 8 - $\underline{50\text{g of water}} \times 8^\circ\text{C} \times \frac{1 \text{ cal}}{1 \text{ g water } 1^\circ\text{C}} = 400$ cal.

Exercise 9 - a. $50 \text{ g ice} \times \frac{80 \text{ cal}}{1 \text{ g ice}} = 4000$ cal.

b. $50 \text{ g water} \times 100^\circ\text{C} \times \frac{1 \text{ cal}}{1 \text{ g water}} = 5000$ cal.

c. $50 \text{ g water} \times \frac{540 \text{ cal}}{1 \text{ g water}} = 27{,}000$ cal.

d. 4000 cal to melt the ice
5000 cal to raise the temperature 100°C
27000 cal to vaporize the water
36000 cal - TOTAL

Exercise 10 - $8 \text{ g water} \times \frac{540 \text{ cal}}{1 \text{ g water}} = 4320$ cal to condense steam.

$8 \text{ g water} \times 100^\circ\text{C} \times \frac{1 \text{ cal}}{1 \text{ g water } 1^\circ\text{C}} =$ 800 cal to cool water to 0°C.

$8 \text{ g water} \times \frac{80 \text{ cal}}{1 \text{ g water}} = 640$ cal to freeze water.

5760 cal total heat removed.

Exercise 11 - Since: $2H_2O \xrightarrow{\text{electrolysis}} 2H_2 + O_2$, twice as much volume of H_2 would be formed. The formula above shows 2 hydrogens for every oxygen atom.

Exercise 12 - False. Sea-water is unfit for human consumption and too corrosive for many industrial uses because it contains large quantities of dissolved salts.

Exercise 13 - Parts per million parts. For example - grams per million grams, lbs. per million lbs., etc.

Exercise 14 - a. NaCl

b. One

c. 23 for Na
35 for Cl

d. $\frac{Cl}{Na} = \frac{35}{23} \approx 1.5$

Exercise 15 - Similar to or approximately.

Exercise 16 - $10{,}500 \text{ ppm Na} \times \frac{35 \text{ ppm Cl}}{23 \text{ ppm Na}} = 16{,}200 \text{ ppm}$

or $10{,}500 \text{ ppm Na} \times \frac{1.5 \text{ ppm Cl}}{1 \text{ ppm Na}} = 16{,}200 \text{ ppm}$

Exercise 17 - 10,500 ppm Na + 16,200 ppm Cl =
26,700 ppm NaCl

Exercise 18 - $2.67\% \text{ NaCl} = \frac{2.67}{100} = \frac{2.67 \times 10^4}{100 \times 10^4} = 2.67 \times 10^4$ ppm NaCl

mol. wt. of NaCl = 22.99 + 35.45 = 58.44

Fraction of Na in NaCl = $\frac{22.99}{58.44} = .3934$

$2.67 \times 10^4 \times .3934 = 1.0500 \times 10^4$
= 10,500 ppm of Na in sea-water

Exercise 19 - total % of salts = 3.5%
total % of NaCl = 2.7%
% salts other than = 0.8% (less than 1%) NaCl

Exercise 20 - a. $(5280 \text{ ft.})^3 = (1 \text{ mile})^3$

We haved cubed each side of an equality and maintain the equality.

b. $(5.28 \times 10^3)^3 = 147.2 \times 10^9$ cu. ft.

c. $147.2 \times 10^9 \times 62.4 = 9.185 \times 10^{12}$ lbs.

Exercise 21 - a. We found that 1 cubic mile of water was equal to 1.47×10^{11} cu. ft. or 9.18×10^{12} lbs. Since sea-water contains, $\frac{1350 \text{ lbs Mg}}{1\text{x}10^6 \text{ lbs } H_2O}$, we can calculate the weight of Mg in the cubic of sea-water.

$$\frac{1350 \text{ lbs Mg}}{1\text{x}10^6 \text{ lbs } H_2O} \text{ x } 9.15\text{x}10^{12} \text{ lbs } H_2O = 12.5\text{x}10^9 \text{ lbs Mg}$$

b. $$\frac{12.5\text{x}10^9 \text{ lbs}}{} \text{ x } \frac{1 \text{ ton}}{2000 \text{ lbs}} = 5.5 \text{ million tons Mg}$$

Exercise 22 - The mining of the seas could destroy sea life and shore lines for great distances, unless suitable care is taken, just as strip mining has laid waste to great areas of land. However, if properly designed, this need not be the case.

Exercise 23 - The answer to this question is in the body of the study guide.

THE THREE STATES OF MATTER

With Emphasis on the Physical Nature of Water

SUMMARY

This mini-course reviews ideal gas law calculations and uses these to establish the quantity of water in the atmosphere. In addition, three states of matter are reviewed with respect to water, including the energy changes involved in converting one state to another.

RATIONALE

Laying the ground work for any study can be relatively routine. On the other hand, the understanding of water in all of its physical states is obviously important, and hopefully reasonably interesting. Much of the information and data covered in this Study Guide will be used throughout our study of water chemistry, so the student is urged to master this mini-course.

ACKNOWLEDGEMENTS

The author appreciates the experience and skill of Dr. Joe Allen, Clemson University, for numerable suggestions that have been included herein.

PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. State Avogadro's number.

2. Use molecular formula and periodic chart to interconvert between grams and moles.

OBJECTIVES

At the end of this mini-course the student should be able to:

1. Define:
   - Gas
   - Liquid
   - Solid
   - Vapor pressure
   - Boyle's Law
   - Charles' Law
   - Avogadro's Number
   - Heat Capacity
   - Heat of fusion
   - Heat of vaporization
   - Amorphous solids
   - Crystalline solids

2. Given a temperature in degrees centrigrade, convert to degrees Kelvin, and vice versa.

3. Use the ideal gas law to determine pressure, volume, temperature, or number of moles when given any three of the four values. (The student must memorize the value of R.)

4. Use a vapor pressure table and the percent humidity to determine the pressure of water in the air at any given temperature.

5. Describe what happens to the density of water as the temperature is varied near $0^{\circ}C$.

6. State the values of heat of fusion, heat of vaporization and specific heat of water from memory. Use these to calculate the energy required to convert water from one state to another.

7. State from memory the six crystal systems.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. A substance which assumes the shape and volume of its container is called: (1) a gas, (2) a liquid, (3) a solid, (4) amorphous, (5) crystalline.

2. The number of molecules which would occupy 22.4 l at 0°C and 1 atm pressure is ________________.

3. How many molecules would occupy 1 liter of gas at STP?

4. A solid which has no definite pattern of atoms is called: (1) crystalline, (2) hexagonal, (3) amorphous, (4) cubic, (5) liquid.

5. What is the temperature in °C which represents 323°K?

6. What pressure would be exerted by 2 moles of N_2 gas at 100°C and occupying a volume of 10 liters?

7. Use Table I to calculate the pressure of water vapor at 30°C and 60% humidity.

8. When water freezes the volume: (1) decreases (2) increases, (3) remains the same.

9. As water is cooled from 30°C to 4°C the volume (1) decreases, (2) increases, (3) remains the same.

10. Calculate the energy required to convert 10 grams of ice at 0°C to water at 30°C.

11. How many calories are released when 20 grams of steam at 100°C are converted to liquid at 100°C.

12. State from memory the six crystal systems.

READING LIST

Eisenberg, D., and W. Kauzmann, The Structure and Properties of Water, Oxford University Press, New York, 1969.

I. INTRODUCTION

Water, like most chemicals, occurs in three physical forms: gas, liquid, and solid. Since water is our main concern of study, attention will be focused primarily upon it, but the student should remember that all gases are somewhat similar to one another, different liquids obey the same laws to some extent, and solids have much in common.

II. GASES

It is quite helpful and surprisingly valid to consider the properties of an ideal gas since, under normal conditions of temperature and pressure, it differs but slightly from a real gas.

Exercise 1

What is an ideal gas?

(Answer below.)

An ideal gas is viewed as being composed of particles that are so small that they have zero dimensions. As will be shown below this isn't far from the truth: an ordinary gas molecule is very, very small. Ideal gas particles are said to have no attraction for one another, such as Van der Waal's forces. Actually, real gas particles have little attraction for one another except when they are brought close together due to low temperatures and/or high pressures.

In other respects, the ideal gas is quite like real gases as viewed by the kinetic theory of gases which looks upon gases as being made of (1) large numbers of very small particles, separated by relatively large distances, (2) the particles move in constant random motion, (3) gas pressure is due to the bombardment of the walls of the containing vessel by the gas particles contained therein, (4) a volume of gas completely fills the containing vessel, (5) gases mix in all proportions and never separate; that is, all gases are completely soluble in one another, (6) collisions between gas particles are perfectly elastic - that is, no energy is lost or gained when a gas particle (real or ideal) strikes another gas particle or the walls of the containing vessel.

Exercise 2

Elaborate on what is meant by "an elastic collision."

(Answer below.)

This latter statement introduces a concept that the science student must be willing to accept in larger and larger doses as he studies the world of tiny objects - atoms and molecules. They just don't obey the same laws as those which apply to microscopic objects.

For example, the above statement that says, "collisions between gas particles are perfectly elastic" really says that gas particles are in perpetual motion - and this must be so. If gas particles gradually lost their thermal energy upon collision with themselves or the walls of the containing vessel, this would mean that they would gradually slow down and eventually stop dashing about in random motion. Thus, upon opening King Tut's tomb, we would find a puddle of liquid air on the floor. Since this has never been observed, we conclude that gas particles making up air never lose their energy.

Arriving at and accepting the kinetic theory of gases - and most scientific theories - required many years of trial and error during which numerous other proposals were made only to be discarded because they did not fit the experimental facts. The kinetic theory of gases fits the facts.

Another important hypothesis relating to gases was proposed many years ago by an Italian physicist names Avogadro (1776-1856). He stated that equal volumes of different gases under identical conditions of pressure and temperature contain the same number of molecules. There was no way for him or anyone else to prove or disprove this "educated guess" until long after Avogadro's death. He has been honored by naming a much used and important scientific constant: Avogadro's number. As related to gases, this is the number of molecules contained in one mole of any gas at standard conditions of temperature and pressure - that is

$$T = 273^{\circ}\ K \text{ and } P = 1 \text{ atmosphere.}$$

Exercise 3

What is the value of Avogadro's number?

Written this way, the hugeness of the number loses its significance. To gain some perspective as to how big this number really is, let us calculate the weight of 6.02×10^{23} grains of sand, assuming that each grain weighs 0.001 grams.

$$6.02 \times 10^{23} \times 0.001 = 6.02 \times 10^{20} \text{ grams}$$

$$6.02 \times 10^{20} \div 454 = 1.33 \times 10^{18} \text{ pounds}$$

$$1.33 \times 10^{18} \div 2000 = 6.66 \times 10^{14} \text{ tons}$$

Suppose a ten-ton truck hauled away a load of sand every ten minutes, 24 hours a day, 365 days a year. The truck would haul:

$$10 \times 6 \times 24 \times 365 = 5.26 \times 10^{5} \text{ tons a year.}$$

A thousand such trucks would haul:

$$5.26 \times 10^{5} \times 1000 = 5.26 \times 10^{8} \text{ tons/1000 trucks/year}$$

$$6.66 \times 10^{14} \div 5.26 \times 10^{8} = 1.27 \times 10^{6} \text{ years}$$

It would thus take 1000 trucks, each hauling ten tons of sand every ten minutes, over one million years to haul 6.02×10^{23} grains of sand. Avogadro's number is not to be taken lightly - that is, with a grain of sand.

III. THE IDEAL GAS LAW

In the mid 1600's, Robert Boyle's experiments with gases showed that at constant temperature the volume of a gas varies inversely with the pressure. That is, the volume of a gas decreases if the pressure is increased.

More that a hundred years later, Jacques Charles showed that at constant pressure the volume of a gas varies directly with the temperature. Another hundred years passed before a glass capillary tube of uniform bore was produced, from which an accurate thermometer could be made. With this, quantitative measurements showed that a flask containing 273 ml of a gas at 0°C. and 1 atmosphere pressure, decreased to 272 ml at -1°C. This trend continues to extremely low temperatures - that is, the volume decreased 1 ml per 1° C. drop in temperature. Extrapolating this indicated that the volume should be zero at -273°C. This turns out to be the case (See Figure I) and it is an extremely remarkable law of nature. So far as is known, temperature has no upper limit, but we believe that it is impossible for anything to be colder than -273.15°C. which is called "absolute zero."

Almost all gas problems are calculated using the positive temperature scale proposed by Lork Kelvin:

$$\text{Absolute zero} = 0^\circ \text{ K} = -273^\circ\text{C}.$$

Exercise 4

What is the formula linking degrees Kelvin with degrees Centigrade?

Avogadro's principle states that the volume of a gas is measured by the number of molecules contained therein. Said differently, a mole of H_2 (2g.) has the same number of molecules as a mole of N_2 (28g.) - each has 6.02×10^{23} molecules. Thus the volume of a gas at constant temperature and pressure is directly proportional to the number of moles - n.

Combining the above:

Boyle's Law	$V \propto 1/P$
Charles' Law	$V \propto T$
Avogadro's Law	$V \propto n$
Altogether	$V \propto \frac{nT}{P}$

$V = R \times \frac{nT}{P}$, where R is the proportionality constant.

Further experiments showed that one mole of a gas at $T = 273^\circ$ K and $P = 1$ atmosphere (known as standard temperature and pressure, or STP) has a volume of 22.414 liters.

Exercise 5

Using this information, calculate the value of R.

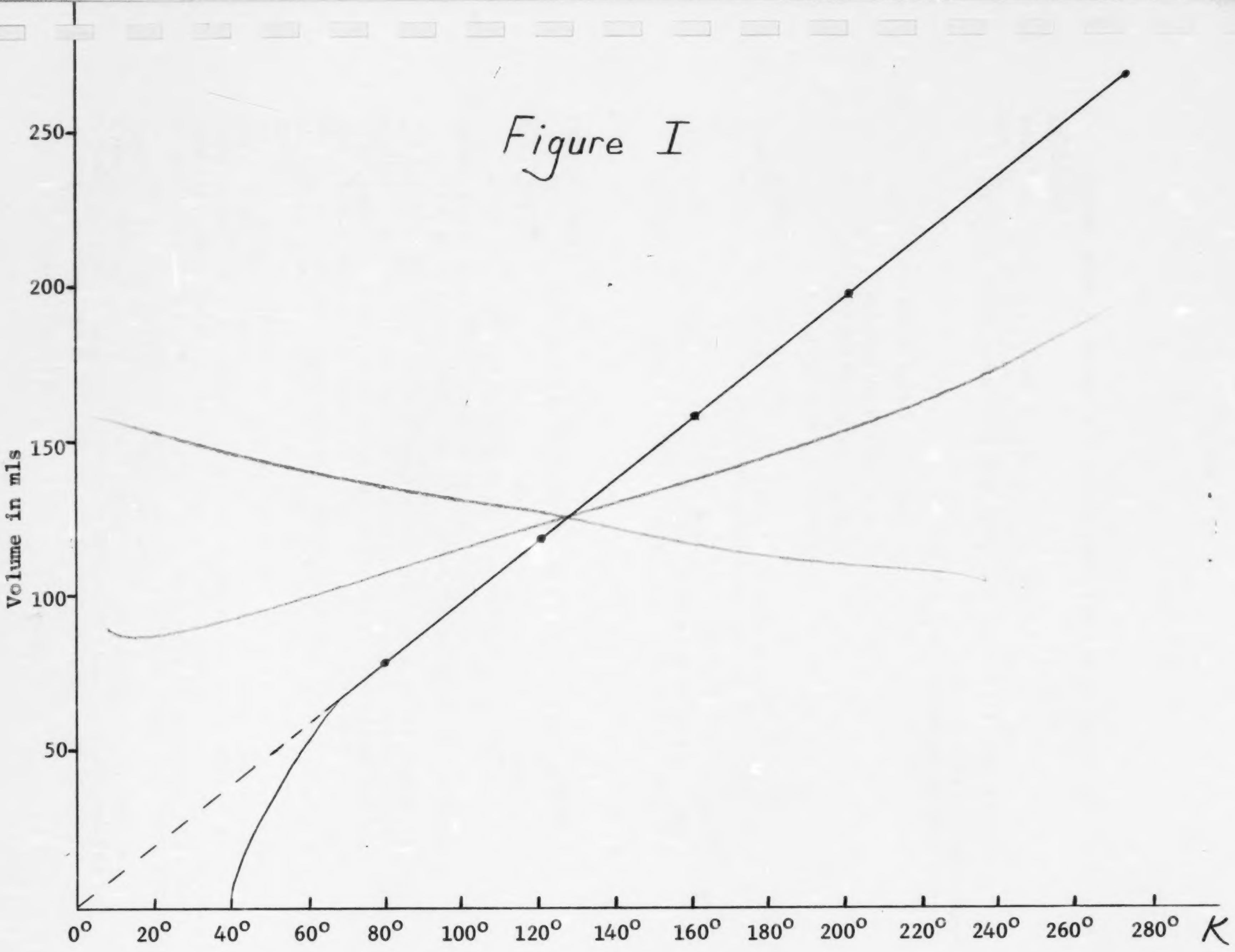


Figure I

Volume in mls
50
100
150
200
250
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
200°
220°
240°
260°
280°
K

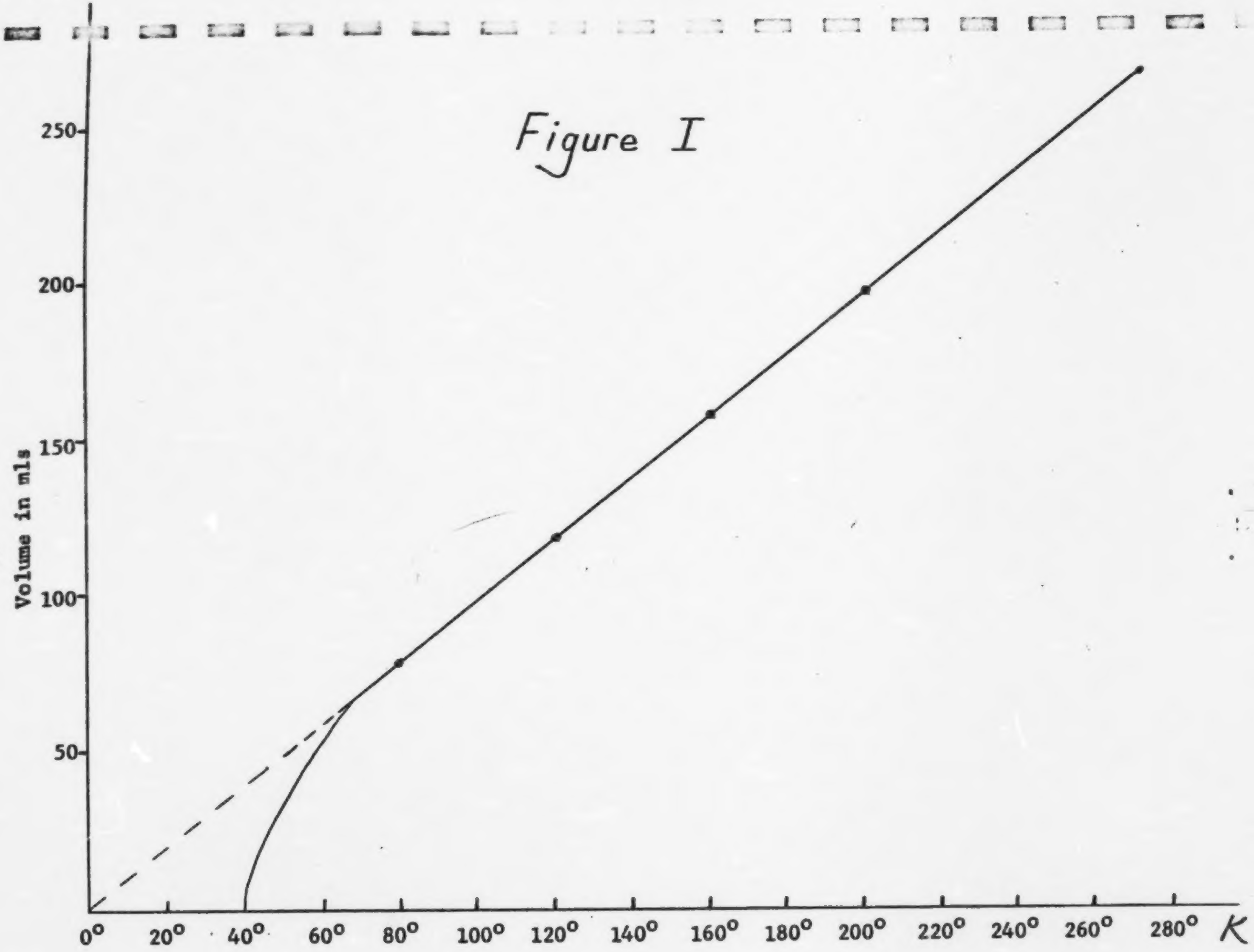


Figure I

Volume in mls
250
200
150
100
50
0°
20°
40°
60°
80°
100°
120°
140°
160°
180°
200°
220°
240°
260°
280°
K

The ideal gas law is thus:

$PV = nRT$ (where $R = 0.08206$ liter atmos./degree K)

P is in atmospheres

V is in liters

T is in K^o

n is the number of moles

If any three of the above four variables are known, the other can be calculated.

Exercise 6

How many grams of water are needed to fill a 5 liter flask with water vapor (gas) as 25°C. and 1 atmospere pressure?

Exercise 7

A cylinder of N_2 weighs 116 lbs. when full. After being used for an experiment it weighs 112 lbs. How many liters were used at a barometer reading of 775 mm. and T = 100°C?

Two other gas laws will be studied later when needed. One is Dalton's Law of partial pressures which states that the total pressure of a gas is equal to the sum of the pressures of each gas in the container. That is:

$$P_{total} = P_1 + P_2 + P_3 + \text{-------}$$

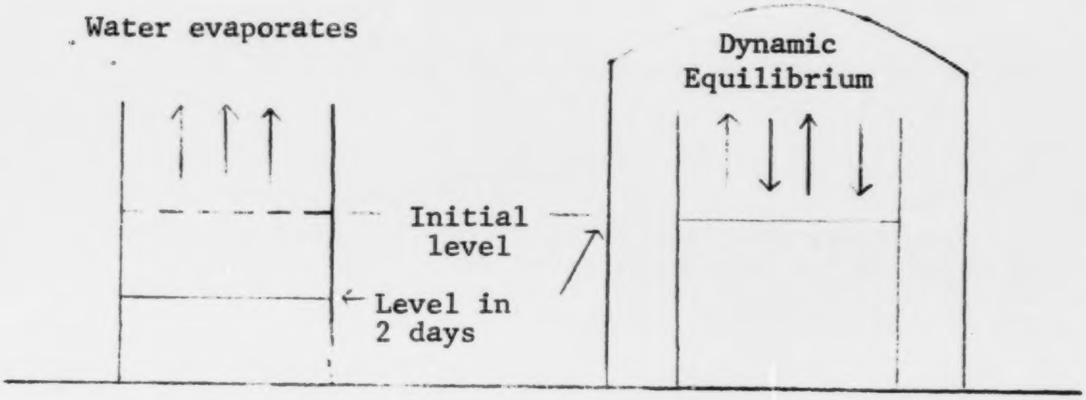
The other is Raoult's Law which deals with the solubility of gases in liquids, such as air in water.

Liquids

A liquid maintains its volume (it does not necessarily fill the containing vessel as does a gas); it takes the contour of the container; it flows; it has a vapor pressure, boiling point, viscosity, refractive index, freezing point, solubility in other liquids, tendency to dissolve solids, heat capacity, heat of vaporization, lowering of freezing point, raising of boiling point - just to mention a few measurable properties. Obviously, there won't be enough time or need to cover all of these. But they are important subjects and all are studied by a major in college chemistry.

It was previously stated that gas particles are extremely small, that they are spearated by relatively large distances, and are in constant random motion. Expressed quantitatively, a water molecules at S.T.P. attains speeds of about 1000 miles per hour, and travels a distance 100 times its own diameter before colliding with another water molecule. If gaseous water molecules are brought close together by increasing the pressure and their speed diminished by lowering the temperature, they eventually become so closely packed that each molecule is loosely associated with many of its neighbors - and this is called the liquid state. "Loosely assocaited" means that the molecules are not rigidly bound to one another on the one hand and not free to dash about in free random motion on the other. Thus the liquid state is intermediate between that of a gas and a solid.

Linking the gaseous and liquid state is a property called "vapor pressure." Suppose a beaker of water were allowed to stand in the labortory for a few days; the water would gradually disappear. If, however, a similar beaker of water were covered - say with a tight-fitting bell jar - the water level in the beaker would not change.



Actually, water molecules do escape from the liquid under the bell jar into the surrounding enclosure, but as they do other gaseous molecules condense back to liquid water. Thus, there is a continuous evaporation and condensation which, as equilibrium, results in a tie race. The tendency - or pressure - of the water to evaporate under equilibrium conditions at a given temperature is called the vapor pressure of the liquid.

It is difficult to measure the vapor pressure of a liquid, but it is an important and much used property. Qualitatively, one observes that a puddle of water evaporates faster on a hot than on a cold day at constant humidity. This means that water molecules escape from the warm water faster than they do from cold water; in escaping, they become gas molecules. The quantitative tendency of a liquid to evaporate is called its vapor pressure. The vapor pressures at various temperatures are available from most pure liquids. For water they are:

TABLE I

°C	Vapor pressure (mm Hg)
0	4.58
10	9.21
15	12.8
20	17.54
25	23.8
30	31.82
40	55.32
50	92.51
60	149.38
70	233.7
80	355.1
90	525.8
100	760.0

The definition of boiling point is when the vapor pressure of a liquid equals the atmospheric pressure. At one atmosphere pressure (760) water boils at 100°C. With a more volatile liquid, such as diethyl ether, the vapor pressure equals 760 mm at 33°C.

Exercise 8

Will water boil above or below 100°C when the atmospheric pressure is 740 mm?

Because water has a vapor pressure at lower temperatures, it evaporates, which means that pure water vapor escapes into the atmosphere leaving behind any dissolved organic and inorganic impurities. From this evaporated water clouds are formed, moisture condenses as rain, and the thirsty world is replenished with clean, fresh water.

By using the ideal gas law, Table I of vapor pressures of water, and several simplifying assumptions, the amount of precipitable water - potential rainfall - in the atmosphere can be calculated.

If the humidity were 100% at 25° C., this would mean that the vapor pressure of gaseous water in the air would be 23.8 mm. Assuming an average atmospheric ceiling of 5,000 feet (about one mile) - which is a valid approximation - the temperature at this height would be about 10°C. lower than at sea-level. The vapor pressure of water at 15°C = 12.8 mm., or a difference of 23.8 - 12.8 = 11.0 mm.

Exercise 9

Plug this into the gas law formula and calculate the moles water/liter.

Exercise 10

Convert the above moles/liter to grams/liter.

Now, let's consider a liter container that is one inch square (2.54 cm. on a side) and of height x cm.

$$(2.54)^2 \times X = 1000$$

$$X = 155 \text{ cm. height of the container}$$

Exercise 11

Convert 155 cm. into feet.

Thus, 10.6×10^{-3} g. of water are present per sq. in. in a 5 ft. column of air under the above assumed conditions.

Exercise 12

How many grams of water are there in an air column 5000 ft. in height under the above conditions?

Since 1 g. water = 1 ml. of liquid water and a column of 1 sq. in. (1" = 2.54 cm) has been used in these calculations.

Exercise 13

How much potential rain does this amount to?

Thus there are about 0.67 in. of potential rain above us under fairly normal atmospheric conditions. Actually, this is very close to the weatherman's predictions. How then can a tropical storm dump so much water on vast areas of the earth? This happens for two reasons: (1) low barometric conditions bring in moisture from large surrounding areas and/or (2) the precipitable rain in the atmosphere is replenished because the storm draws huge amounts of water from the Gulf of Mexico, the Great Lakes and adjoining oceans - as happens in the case of large hurricanes.

For a brief review of some of the other physical properties of water, the student should recall the following since this information will be referred to frequently throughout our study of water chemistry.

Heat Capacity	By definition, one calorie of heat is required to raise 1g. of water by 1° C. (This varies slightly from 0°C. to 100 C.) It takes 0.445 calories of heat to raise 1g. steam 1° C. To reduce the temperature of 1g. of ice by 1° C., .0500 calories must be removed.
Heat of fusion	It requires the removal of 79.4 calories of heat to convert 1g. water at 0° C. to ice at 0° C.
Heat of vaporization	It requires the addition of 540 calories of heat to convert 1g. of water at 100°C. to steam at 100° C.
Freezing point lowering	The addition of 1 mole of a non-ionizable soluble substance to 1000g. of water reduces the freezing point by 1.86° C. Examples of soluble non-ionizable substances are methanol and glycol.
Boiling point elevation	The addition of 1 mole of a soluble non-ionizable substance to 1000g. of water raises the boiling point by 0.512° C.

Exercise 14

Calculate the energy required to do each of the following:

a. Melt 1 pound of ice at 0°C.

b. Evaporate 1 ton of water at 100°C.

c. Convert 100 grams of ice at -50°C to steam at 250°C.

Solids

The kinetic view of matter is that, as the temperature of a substance is lowered, the energy of the molecules comprising the substance is correspondingly reduced. Thus as the temperature of gaseous water molecules is reduced, their motion is proportionately restricted until they become liquid water. Further lowering of the temperature removes still more kinetic energy until the water molecules form a crystal - ice is formed. Ice is a solid.

A solid has a fixed shape and volume, thus it does not fill a container as does a gas, or assume the shape of the containing vessel as do gases and liquids. In general, there are two kinds of solids: (a) amorphous and (b) crystalline.

Amorphous solids have no definite structure; their molecules are not arranged in a precise pattern. Glass is an amorphous solid, so are wax, gels, certain plastics, etc. Amorphous solids are not of primary importance to water chemistry.

Exercise 15

Identify each of the following as (1) liquid, (2) amorphous solid, (3) crystalline solid. Look at the samples available if needed.

a. ice - ____________________

b. wood - ___________________

c. sand - ___________________

d. table salt - ______________

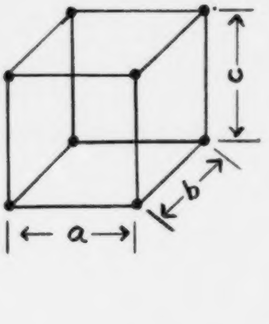
e. glass - __________________

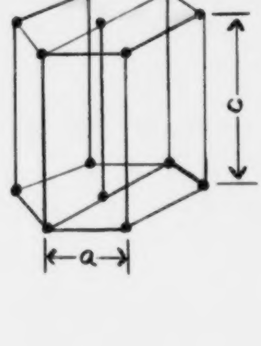
f. hard plastic - ____________

Ice is crystalline and beautiful to behold until too many snowflakes clog our highways and an ice storm breaks down trees and power lines.

All crystalline solids occur as one of six crystal systems. This means that the atoms or ions comprising the crystal are arranged in one of six - and only six - precise patterns. All crystals - diamond, alum, salt, emerald, quartz, sand, etc., - occur in one of these six systems.

The student should refer to and review a college chemistry text for a detailed description of crystals. He will find that crystals occur as:





Cubic

Sides equal $a = b = c$
All angles = 90°

Hexagonal

Sides $a = b = c$
Angles $\alpha = b = 90^\circ$
$y = 120^\circ$

Tetragonal

Sides $a = b \neq c$
Angles $\alpha = b = y = 90^\circ$

Orthorhombic

Sides $a \neq b \neq c$
Angles $\alpha = b = y = 90^\circ$

Monoclinic

Sides $a \neq b \neq c$
Angles $\alpha = y = 90^\circ$
$b = 90^\circ$

Triclinic

Sides $a \neq b \neq c$
Angles $\alpha = b = y = 90^\circ$

The complexity of crystal structure is such that, as a beginning, discussions are limited to a simple cubic system. Each atom or ion is viewed as (a) occupying one corner of the cube; (b) vibrating within extremely restricted distances and (c) being bound to its neighbors with powerful forces. Under a given set of conditions - usually temperature and pressure - a given substance occurs in one crystalline form only. For instance, all table salt - no matter where it comes from - is a simple cube.

At normal conditions of temperature and pressure, ice crystals are hexagonal. It is apparent from the above sketch that the structure of an hexagonal crystal could be fairly open if the "c" axis is large compared to the other two. This is the case with an ice crystal; in other words, it has what amounts to large holes in it, and therefore has a low density. This is the main reason that ice floats; it has a lower density than water at 0° C. How fortunate this is! If ice were denser than water it would sink to the bottom of the lake, river or ocean. Then more ice would form on the surface and sink until the whole body was solid ice. It is questionable whether life could and would exist on earth if ice did not float on water.

The relative densities of water near the freezing point are:

°C.	Density (g/ml)
0 ice	0.9168
0 water	0.99987
1	0.99993
2	0.99997
3	0.99999
4 (3.98)	1.00000
5	0.99999
6	0.99997
7	0.99993
8	0.99988

Very few crystals are less dense than the liquid from which they are formed, so that ice is an extremely unusual solid. For example, since it is less dense than water, pressure tends to melt ice - such a common happening that it is usually overlooked.

Yet this is why a fluid film forms between the sharp edges of an ice skate and the frozen surface of a lake. Under these conditions, the pressure - which is force per unit area - is great and thus a liquid layer of slippery water enables the skater to glide along with the greatest of ease. Nature is marvelous almost beyond comprehension, but as scientists we are attempting that comprehension.

For example, the polarity and bond angle of the water molecule are the primary reasons for the crystal structure and, therefore, the beauty of the ice crystals.

ANSWERS

A. Pretest

1. (1)
2. 6.02×10^{-23} molecules
3. 2.7×10^{22} molecules
4. (3)
5. 50°C.
6. 6.1 atmospheres
7. 19.1 mm H_2O vapor
8. (2)
9. (1)
10. 1100 calories
11. 10,800 calories
12. See page 56.

B. Study Guide

3. Avogadro's number (n) = 6.0225×10^{23}

4. $^{\circ}K = {}^{\circ}C + 273.15$

5. Substituting these values in the gas law equation:

$$PV = nRT$$
$$1 \times 22.414 = 1 \times R \times 273$$
$$R = 0.08206 \text{ liter atoms./degree mole}$$

6. $1 \times 5 = \frac{m}{18} \times 0.08206 \times 298$ $\qquad$ $\text{moles} = \frac{\text{Mass}}{\text{Mol. wt.}}$

$m = 3.69$ g. water $\qquad$ $n = \frac{m}{w}$

7. 116 - 112 = 4 lbs.; 4 x 454 = 1816 g. N_2 used.

$$\frac{775}{760} \times V = \frac{1816}{28} \times 0.08206 \times 373$$
$$V = 1950 \text{ liters}$$

8. Below 100° C. because a lower temperature is required to give a vapor pressure of 740 mm.

9. $PV = nRT$

$$\frac{11.0}{760} \times 1 = n \times 0.082 \times 298$$
$$n = 5.90 \times 10^{-4} \text{ moles water/liter.}$$

10. $5.90 \times 10^{-4} \times 18 = 10.6 \times 10^{-3}$ g. water/liter.

11. $155 \text{ cm} = \frac{155}{2.54} = 60.8 \text{ in.}$

$$\frac{60.8}{12} = 5 \text{ feet}$$

12. $10.6 \times 10^{-3} \times 1000 = 10.6$g. water in a column 5000 ft. in height.

13. $(2.54)^2 \times X = 10.6 \text{ cm}^3$ $\qquad$ $(1g = 1 \text{ cm}^3)$

$$X = 1.64 \text{ cm} = 0.65 \text{ inches}$$

14. a. $1 \text{ lb.} \times \frac{454 \text{ g.}}{1 \text{ lb.}} \times \frac{79.4 \text{ cal.}}{1 \text{ g.}} = 36{,}000 \text{ cal.}$

b. $1 \text{ ton} \times \frac{2000 \text{ lb.}}{1 \text{ ton}} \times \frac{454 \text{ g}}{1 \text{ lb.}} \times \frac{540 \text{ cal.}}{1 \text{ g.}} = 4.9 \times 10^{8} \text{ cal.}$

c. Heat ice to 0°C:

$$100 \text{ g.} \times 0.500 \frac{\text{cal.}}{\text{g} \times \text{deg.}} \times 50 \text{ deg.} = 2500 \text{ cal.}$$

Heat water from 0°C to 100°C:

$$100 \text{ g.} \times 1.00 \frac{\text{cal.}}{\text{g} \times \text{deg.}} \times 100 \text{ deg.} = 10{,}000 \text{ cal.}$$

Evaporate water at 100°C:

$$100 \text{ g.} \times 540 \frac{\text{cal.}}{\text{g.}} = 54{,}000 \text{ cal.}$$

Heat steam from 100°C to 250°C:

$$100 \text{ g.} \times 0.445 \frac{\text{cal.}}{\text{g} \times \text{deg.}} \times 150 \text{ deg.} = 6700 \text{ cal.}$$

TOTAL = 81,200 cal.

15. a. (3) crystal
    b. (2) amorphous
    c. (3) crystal
    d. (3) crystal
    e. (2) amorphous
    f. (2) amorphous

(These are not always clear-cut; glass is sometimes called an extremely viscous liquid, and some plastics may have crystalline properties.)

WATER AND THE ENGINEER

SUMMARY

Related to water, engineering is an old and impressive profession. The reason is compelling: potable water is essential to mankind, and the denser the population the greater and more complex are the problems that must be solved by the engineer - then and now.

It is a relatively simple matter to pour water from a pitcher to a glass, turn a spigot, or flush a toilet. The average person has no appreciation whatsoever as to how and why any of their public utilities operate. The purpose of this mini-course is to help the student understand some of the basic engineering problems and principles of handling water.

ACKNOWLEDGEMENT

The author is indebted to Mr. N. C. Vasuki, Director of Environmental Control of the State of Delaware for outlining the general format of this Study Guide and providing general guidance in its preparation.

PREREQUISITES

Before beginning this mini-course, you should be able to:

1. Use trigonometric expressions to calculate the volume and area of a pipe of given dimensions if the pipe is partially filled.

2. Convert from ft^3/sec. to gallons/min. for water flow.

3. Derive mathematical equations using integral calculus. (Actually, you can survive if you accept the derivation.)

4. State that 7.48 gal. = 1 ft^3.

5. State that acceleration due to gravity (g) = 32.2 ft/sec^2.

OBJECTIVES

At the completion of this mini-course, you should be able to:

1. State that the engineer normally uses the English System of measurement.

2. State that one atmosphere of pressure equals 14.7 lb/in^2 or 34 ft of water.

3. Use Bernoulli's equation to calculate the water pressure in a given system when given the appropriate data, such as relative heights, pipe diameter, etc. (The equation need not be memorized and will be provided to you.)

4. Use the equation: $F = \frac{w \partial L^2}{2}$ to calculate the force, in pounds, exerted upon a dam of given dimensions.

5. Describe: (a) The operation of a Venturi meter and state how the design minimizes pressure

(b) The use of an orifice to measure water flow and contrast the use of the orifice to the Venturi meter.

(c) The use of a Rotameter.

6. Memorize and use the Chezy formula for calculating the velocity of water in a pipe under the influence of gravity, when given the coefficient, C , the slope, and the hydraulic radius of a pipe.

7. Describe the operation of a current meter to measure the flow of a stream, including advantages, disadvantages, choice of location, and calibration.

8. Describe the operation of:

a. A positive pressure pump.

b. A positive displacement pump.

c. Gate valves.

d. Globe valves.

The discription should include uses for these items and limitations for those uses.

PRETEST

1. Calculate the pressure exerted in a 12" pipe when 400 gal/min. are flowing through the pipe from a water tank 200 ft. above this pipe. (Use the equation found on page 66.

2. What is the height of a column of water which can be supported by 1 atmosphere of pressure?

3. Calculate the force exerted on a dam which is 200 ft. wide and has a water depth of 45 ft.

4. Describe the operation of each of the following:

   a. A Venturi meter.
   b. An orifice for measuring water flow.
   c. Rotameter.
   d. A current meter in a stream.
   e. A positive pressure pump.
   f. A positive displacement pump.
   g. Gate valves.
   h. Globe valves.
   i. V-Notch Weir

5. What is the flow rate in gal/min. for a 5 ft. diameter pipe half filled with water? $R_H = 1$, $C = 99$, and the slope is 0.8 ft. per 100 ft.

WATER AND THE ENGINEER

People have always gathered - and will always gather - where potable water is available. Early civilizations such as Mesopotamian, Indian, Chinese, and Egyptian all centered on the banks of great rivers - just as we do today. Rivers have often been and still are well defined boundaries between kingdoms, nations and states. Even today, states and individuals bitterly contest water rights, for without adequate water resources, we cannot live as a nation or as an individual.

Related to water, engineering is a far older profession than chemistry - even alchemie. The reasons are obvious: water has always been and will always be essential to mankind for drinking, cooking, washing, watering livestock, growth of crops, commerce and industry. To meet these needs and demands, the engineering feats of the ancients are most impressive. Some fine examples of great engineering achievements are: 1) the Roman aqueducts near Rome, 2) the stream gage near Alexandria in Egypt, and 3) the famous public baths of Mahanjadaro along the Indus Valley in Pakistan. Water has been the mainstay of civilizations throughout history.

At the risk of over-simplification, one of the primary roles of the engineer - then and now - is to transport water from one place to another. This may be many miles, or from one point in a treatment plant to another. Transporting water from source to destination may be simple or complex, free or expensive, obvious or hidden. The average person has little appreciation as to how and why any of their public utilities operate - how and why pure drinking water flows from a faucet, or what happens when wastewater disappears down the drain. The purpose of this mini-course is not to compress a degree in engineering into one easy lesson, but to help the student understand some of the basic engineering problems and principles that bring pure water to and take used water from people: people in cities, towns and remote urban areas.

In the first place, water runs down hill, and when and where this happens, the process is usually simple, free and obvious. But not necessarily so. The cost of trying to prevent floods along the Mississippi River and its tributaries is tremendous as Ole Man River runs down hill. The building of aqueducts to transport water from up-state New York to New York City is a huge and expensive engineering feat.

If water only ran down hill, the world would really be in serious trouble. Actually, it is extremely doubtful that we would have a world as we know it, if water did not evaporate to form clouds and thence rainfall, for this is the world's chief source of pure water, as well as a main source of harnessable energy. In a sense and of great practial importance, water "runs uphill" when it evaporates, so that clouds can be formed that result in rainfall.

Civil engineering is the basic background of today's sanitary engineer. The responsibility of the water chemist is to cooperate with the engineer in order to remove impurities from water. For example, the settling out of solids is an engineering problem, but the formation of particles large enough to settle under a given set of conditions may be dependent upon the adjustment of pH and/or the addition of chemicals - which is the domain of the chemist. In other words, the engineer and chemist are on the same team, and they both recognize water as an amazing fluid.

The behavior of water - whether still or in motion - is dependent upon its unusual physical and chemical properties. Before considering some of the engineering aspects of handling water. let us define the units of measurement used by the engineer, since these are an essential part of his language. Just as the chemist uses grams, calories, degrees centigrade, etc., the sanitary engineer works with the so-called English system, since it is the one now accepted in the United States. In this system, the units usually used are:

Symbol	Dimension	Definition
M	lb.	*Mass
ρ	lb./ft.^{3}	Density - mass per unit volume
Sp. Gr.	None	Ratio of the density of a substance to the density of water at 4° C.
P	lbs./in.^{2}	Pressure - pressure at sea level is 14.7 lbs./in.^{2}. This equals a mercury column 29.92 inches in height.

Bernoulli's Equation

Maintaining adequate and constant water pressure is one of the engineer's main problems. When water flows freely and with good pressure from a spigot, this means that some engineer is on duty seeing to it that a complicated system of tanks, mains, valves, pumps, pipes and reservoirs are working properly.

The most common and well known way of maintaining adequate and constant water pressure - for cities, towns and isolated homes - is by use of elevated water tanks or reservoirs. Lest we become too enamored with the achievements of modern science it was Daniel Bernoulli, a Swiss physicist and mathematician, who in 1738 proposed the formula used by today's engineer for calculating water pressure under various conditions. Bernoulli's equation expresses the energy difference that occurs when fluids (liquids or gases) flow from one point to another. This basic mathematical expression is based on the first law of thermodynamics: energy cannot be made or destroyed. Therefore, the energy at the initial point in a process must equal the energy at the final point in the process; during the transition from the initial to the final stage, three kinds of energy are involved:

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*Actually, a pound is a unit of weight; that is, a pound is the force with which a unit of mass is attracted to the earth. At, or near, sea level, mass and weight are numerically equal.

1) Potential energy - height - H (feet)

2) Kinetic energy - $\frac{V^2}{2g}$ (feet)

3) Energy due to pressure - $\frac{P}{\partial}$ (feet)

Bernoulli's equation states that the energies at the initial and final stages are

$$\text{Initial} \quad - \quad E_1 = H_1 + \frac{(V_1)^2}{2g} + \frac{P_1}{\partial}$$

$$\text{Final} \quad - \quad E_2 = H_2 + \frac{(V_2)^2}{2g} + \frac{P_2}{\partial}$$

Since energy cannot be made or destroyed, the initial and final energies must be equal, if frictional losses are ignored. Thus:

$E_1 = E_2$ and therefore

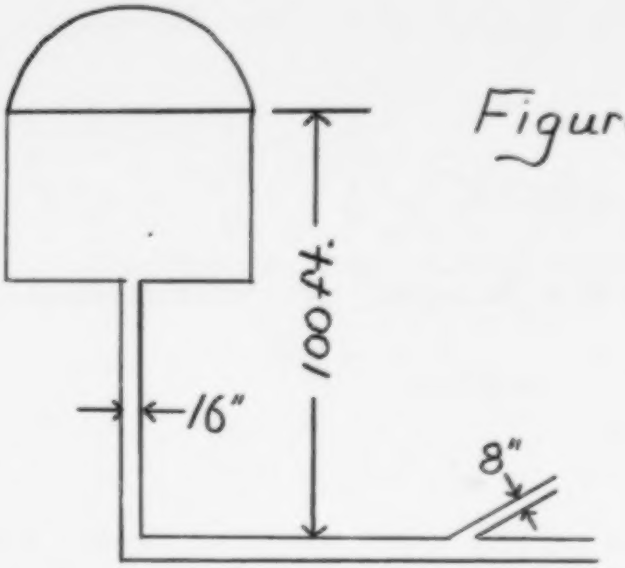
$$H_1 + \frac{(V_1)^2}{2g} + \frac{P_1}{\partial} = H_2 + \frac{(V_2)^2}{2g} + \frac{P_2}{\partial}$$

The student should have recognized immediately that H_1 and H_2 are expressed as feet, and this is not a measure of energy.

Exercise 1

Show that $V^2/2g$ and P/∂ also have the dimensions of feet. Actually, one commonly used unit of energy is foot-pounds; that is, the pounds of water involved But for any one situation involving pressure at a constant height, the amount of water is a constant that cancels out of the calculations.

Let us now apply Bernoulli's equation to a practical situation. Suppose the top of a water tank in 100 feet above the ground and is maintained full (or near full) all the time. The tank is on top of a 16" water main, off which an 8" line at ground level leads to a number of homes. On the average, these homes consume 50 gal./min. of water; what is the water pressure in the 8" line? Schematically the system may be viewed as:



In this problem:

H_1 = 100 ft., elevation of the water in the tank.

H_2 = 0 ft., ground level.

V_1 = 0 ft./sec. velocity of water at top of tank.

V_2 = velocity of water at bottom of tank.

d_2 = diameter of lower pipe = 8" = 2/3 ft.

A_2 = cross sectional area of lower pipe.

Q = volume of water flowing through pipe = 50 gal./min.

$A_2 = \pi r^2 = 3.14 \times (1/3)^2 = 0.349 \text{ ft.}^2$

Q = 50/60 = 5/6 gal./ sec.

$Q = \frac{5/6 \text{ gal./sec.}}{7.5 \text{ gal./ft.}^3} = 0.111 \text{ ft.}^3/\text{ sec.}$

$Q = A_2V_2$ (The quantity of water flowing through a pipe is equal to the cross sectional area of the pipe times the velocity of the water flowing through the pipe.)

$$0.111 \text{ ft.}^3/\text{sec.} = 0.348 \text{ ft.}^2 \times V_2$$

$$V_2 = 0.318 \text{ ft./sec.}$$

Substituting these values in Bernoulli's equation:

$$H_1 + \frac{(V_1)^2}{2g} + \frac{P_1}{\partial} = H_2 + \frac{(V_2)^2}{2g} + \frac{P_2}{\partial}$$

$$100 + 0 + \frac{P_1}{\partial} = 0 + \frac{(0.318)^2}{2 \times 32.2} + \frac{P_2}{\partial}$$

$$\frac{P_2 - P_1}{\partial} = 100 - \frac{(0.318)^2}{2 \times 32.2} = 100 \text{ ft.}$$

$$P_2 - P_1 = 100 \times \partial = \frac{100 \text{ ft.} \times 62.4 \text{ lbs./ft.}^3}{144 \text{ in.}^2/\text{ft.}^3}$$

$$P_2 - P_1 = 43.3 \text{ lbs./in.}^2$$

Since the pressure at the top of the tank is zero, $P_1 = 0$, and $P_2 = 43.3$ lbs./in.^{2} = the pressure in the 8" line.

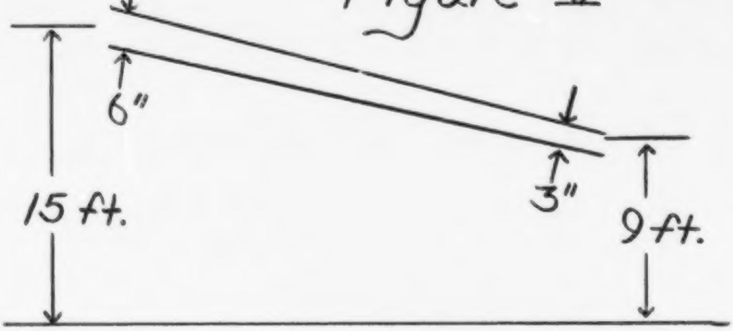
Exercise 2

Now you try solving a problem using Bernoulli's equation. Calculate how high a water tower must be in order to yield a pressure of 20 lb./in.^{2} at a faucet connected to a 6" water main at ground level. Also assume that the pressure at the higher level is 5 lb./in^2.

A slightly different problem using Bernoulli's equation, would be the case of a sluice supplying water to a textile plant. Suppose water is flowing through an inclined pipe which is 6" in diameter at the upper level and 3" in diameter at the lower end.

The quantity of water flowing through the pipe is 450 gal./min. The top end of the pipe is 15 feet above ground level, and the lower end in 9 feet above the ground. Find the difference in pressure between the top and bottom of the pipe.

Figure II



In this problem let:

H_1 = elevation of higher end of pipe = 15 feet

H_2 = elevation of lower end of pipe = 9 feet

d_1 = diameter of higher end of pipe = 6" = 0.5 feet

d_2 = diameter of lower end of pipe = 4" = 0.33 feet

A_1 = cross sectional area of higher end of pipe area =
$3.14 \times r^2 = 3.14(0.25)^2 = 0.196$ ft.^{2}

A_2 = cross sectional area of lower end of pipe area =
$3.14 \times r^2 = 3.14(0.167)^2 = 0.087$ ft.^{2}

Q = volume of water flowing through pipe = 450 gal./min.

$Q = \frac{450 \text{ gal./min.}}{60 \text{ sec./min.}} = 7.5$ gal./sec.

$Q = \frac{7.5 \text{ gal./sec.}}{7.5 \text{ gal./ft}^3} = 1$ ft. sec.^{3}/sec.

$Q = A_1V_1 = A_2V_2$

1 ft.^{3}/sec. = 0.196 ft.^{2} x V_1; V_1 = 5.10 ft./sec.

1 ft.^{3}/sec. = 0.087 ft.^{2} x V_2; V_2 = 11.49 ft./sec.

Substituting these values in Bernoulli's equation:

$$H_1 + \frac{(V_1)^2}{2g} + \frac{P_1}{\partial} = H_2 + \frac{(V_2)^2}{2g} + \frac{P_2}{\partial}$$

$$15 = \frac{(5.10)^2}{2 \times 32.2} + \frac{P_1}{\partial} = 9 + \frac{(11.49)^2}{2 \times 32.2} + \frac{P_2}{\partial}$$

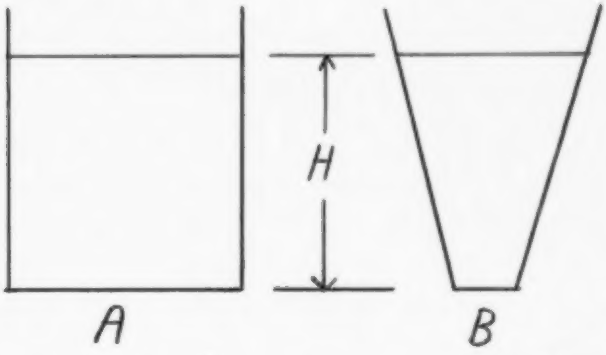
$$15.40 + \frac{P_1}{\partial} = 11.05 + \frac{P_2}{\partial}$$

$$\frac{P_2 - P_1}{\partial} = 15.40 - 11.05 = 4.35 \text{ ft.}$$

$$P_2 - P_1 = \frac{4.35 \times 62.4}{144} = 1.89 \text{ lbs./in.}^2$$

Bernoulli's equation says nothing about the shape of a containing vessel. In other words, if the kinetic energy is zero because there is no flow of water, then the pressure at the bottom of a body of water (tank or reservoir) is dependent only of the depth and density of the water. Thus the water pressures at the bottom of tanks A and B are the same:

Figure III

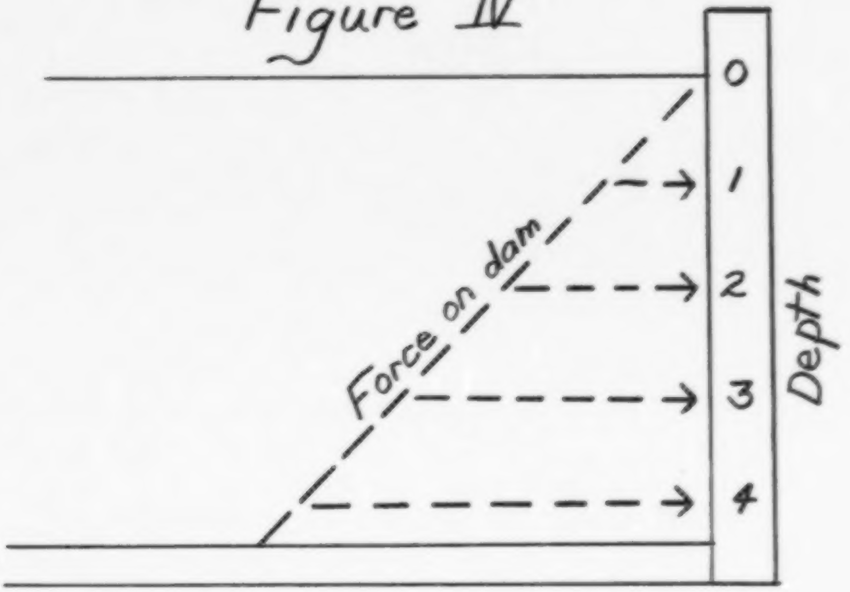


Exercise 3

Calculate the pressure in lbs./in.^{2} at the bottom of a body of water where H = 25 feet.

It also follows from the above, that the pressure on the sides of a containing vessel - or the pressure against a vertical retaining wall with water on one side, such as a dam - is directly proportional to the depth of the water. In Figure IV, the arrows are vectors representing the pressure at different depths. The length of these vectors vary in direct proportion to the depth, which is another way of saying that pressure is directly proportional to the depth of the water.

Figure IV



By the use of moments and calculus, it can be shown that the center of force upon a vertical dam is 2/3 the distance from the surface of the water to the bottom of the dam. Horizontally, the center of force is obviously at the middle of the dam.

Now let's ask the question: how great is the force exerted by water on a dam, retaining wall, or sides of a tank? To derive this formula - or answer this question - requires the use of some simple calculus, which is probably not beyond the scope of many students taking this course. So here goes with some calculus since this is the only way the answer to our question can be obtained. The sketch for this derivation is extremely simple:

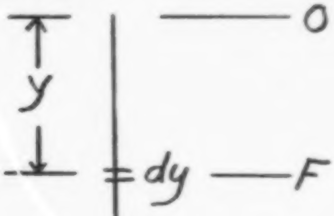


Figure V

What calculus does is to add up all the forces that push against the dam at each increment of depth - dy - from the top to the bottom of the dam. We assume that the width of the dam and the density of water are constants. We know that:

Pressure = force/area, $P = F/A$

Pressure = density x height, $P = \partial \times y$

Thus,

$$F = P \times A \quad \text{(force = pressure x area)}$$

$$dF = P \times dA = P \times W \times dy \quad \text{(area = width x depth)}$$

substituting $P = \partial \times y$

$$\int_0^F dF = W \partial \int_0^L y\,dy$$

$$F = \frac{W \partial L^2}{2} \text{ lbs.}$$

Exercise 4

Insert the proper dimensions to the term in the above equation and show that the force is expressed in pounds.

Exercise 5

Calculate the force exerted against a dam which is 75 feet wide and the water is 20 feet deep.

Measurement of water flow through a pipe

Venturi Meter

The engineer must know how much water is flowing through a pipe. One of the most frequently used devices for doing this is the Venturi Meter; its operation is based on a practical application of Bernoulli's equation.

A Venturi Meter is inserted into a water pipe as follows:

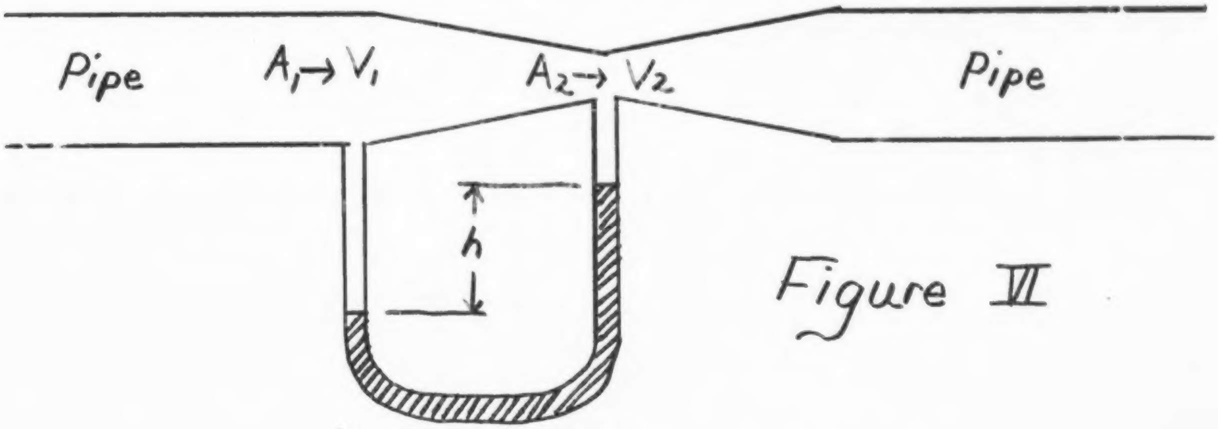


Figure VI

Venturi Meter

As the above sketch shows, a Venturi Meter is a short length of pipe tapering into a narrow throat and tapering back to its original diameter. The taper changes the pressure at the throat from that at the point of entry; these two pressures are measured by the height of water (or mercury) in the two narrow tubes. The difference in these heights is 'h'.

To calculate the flow of water through a pipe, let:

A_1 = area of the larger section

V_1 = velocity of the water in the larger section

A_2 = area of the throat section

V_2 = velocity of water in the throat section

Q = volume of water flowing through the meter

h = difference in height of water in the two tubes

As noted before:

$$Q = A_1V_1 = A_2V_2$$

$$V_1 = \frac{A_2}{A_1} \times V_2$$

From Bernoulli's equation;

$$0 + \frac{(V_1)^2}{2g} + \frac{P_1}{\partial} = 0 + \frac{(V_2)^2}{2g} + \frac{P_2}{\partial} \quad \text{(Potential energy = 0)}$$

$$\frac{P_1 - P_2}{\partial} = \frac{(V_2)^2 - (V_1)^2}{2g} \;; \quad \text{but} \quad \frac{P_1 - P_2}{\partial} = h$$

$$h = \frac{(V_2)^2 - (V_2 \times \frac{A_2}{A_1})^2}{2g} \;; \quad \text{since } V_1 = \frac{A_2}{A_1} \times V_2$$

Solving for V_2;

$$V_2 = \frac{A_1}{\sqrt{(A_1)^2 - (A_2)^2}} \times \sqrt{2gh}$$

Now multiply both sides of the equation by A_2 and remember that $Q = A_2V_2$.

$$Q = A_2V_2 = \frac{A_1 \times A_2}{\sqrt{(A_1)^2 - (A_2)^2}} \times \sqrt{2gh}$$

For any given meter, A_1, A_2 and g are constants so that;

$$Q = C\sqrt{h}, \quad C = \frac{A_1 \times A_2}{\sqrt{(A_1)^2 - (A_2)^2}} \times \sqrt{2g}$$

In real applications, there are always frictional losses, so that by experimentation a correction factor - K - is determined which really doesn't change the Venturi Meter readings very much; on the average K = 0.97. The reason the correction is nearly 1.0 for the Venturi Meter is due to the smooth cone-like narrowing to the throat followed by a similar smooth tapering back to the original diameter of the pipe. Little energy is lost.

Finally:

$$Q = KC\sqrt{h}$$

The use of this equation in a typical problem is fairly easy. For example, calculate the flow in a 6" diameter pipe which has a Venturi throat of 3". The difference in pressure readings is 9 feet. Assume K = 0.95.

$d_1 = 0.5$ feet

$A_1 = 3.14 \times (0.25)^2 = 0.196$ feet^2

$d_2 = 0.25$ feet

$A_2 = 3.14 \times (0.125)^2 = 0.049$ feet^2

$h = 9$ feet

$$C = \frac{A_1 \times A_2}{\sqrt{(A_1)^2 - (A_2)^2}} \times \sqrt{2g}$$

$$C = \frac{0.196 \times 0.049}{\sqrt{(.196)^2 - (.049)^2}}{}_2 \times \sqrt{2 \times 32.2}$$

$C = .406$

$Q = KC\sqrt{h} = 0.95 \times .406 \times (9)^{1/2} = 1.16$ ft.^{3}/sec.

Exercise 6

1.16 ft.^{3}/sec. = how many gallons per minute?

Orifice

An orifice is another simple device, utilizing Bernoulli's equation, that measures the flow of water through a pipe. An orifice is a disk with a hole in it; the disk is held inside the pipe. Tubes for measuring the pressure on both sides of the orifice are similar to those used for the Venturi Meter:

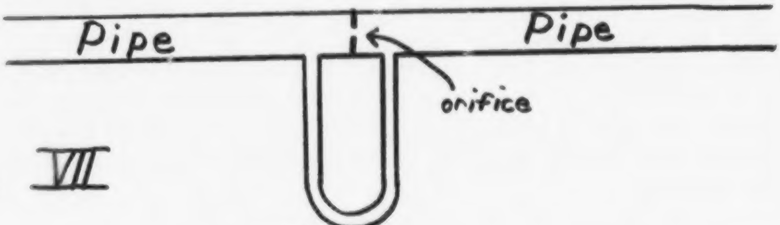


Figure VII

Orifice

In general, an orifice is used in pipes of relatively small diameter where the pressure drop - due to the orifice - is relatively unimportant. For example, a typical correction factor - K - for an orifice might be 0.61, which shows that 39% of the initial pressure was lost due to the water going through the orifice. The engineer says that the orifice causes turbulent flow - eddy currents - which results in loss of pressure; the Venturi Meter's gradual tapering provides for smooth flow and thus very little loss in pressure.

The design of an orifice may vary considerably, but good rules of thumb are to have:

a) the hole in the orifice = 1/5 the pipe diameter,

b) location of the upstream pressure tap = 0.8 x the pipe diameter,

c) location of the downstream pressure tap = 0.4 x the pipe diameter, and

d) the orifice should be made of thin metal, of sufficient thickness to with stand the pressure in the pipe. The metal thickness should be about 1/16" and no thicker that 3/16".

Exercise 7

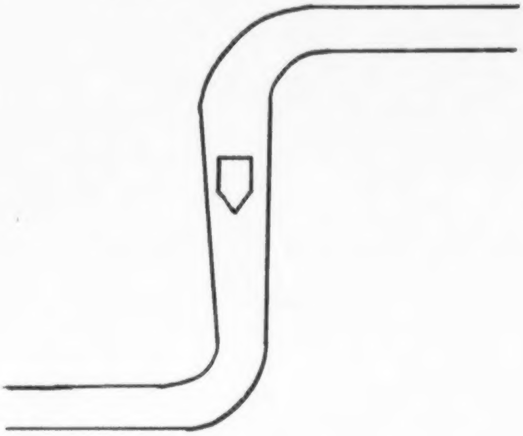
Using the same formula as for the Venturi Meter, calculate the flow of water through a 1-1/4" pipe, having an orifice hole of 1/4" and an upstream pressure tap reading of 7 feet and a downstream pressure tap reading of 2 feet. K = 0.61. Give your answer in ft.^{3}/sec. and gallons per minute.

Rotameter

Perhaps the device most often used for measuring the flow of water through a pipe is a rotameter. Ironically, the name is a misnomer.

A rotameter is simply a float - usually called a plummet - contained inside a slightly tapered vertical glass tube. The flow of water through the tube raises the plummet, and the height of rise is empirically calibrated to indicate the flow of water.

Figure VIII



Rotameter

The plummets in the first rotameters were made with slotted sides so that the plummet rotated due to the flow of water. Experience has shown that such rotation results in inaccurate readings, so the plummet no longer rotates, but the term lingers on.

Water Flow by Gravity in Partially Filled Pipes

Water is not always pumped through pipes; very often it is made to run down hill through a pipe. It is for this reason that an area is carefully surveyed before a sewer line is laid, so as to take advantage of the natural drainage contour of the land. Sewer pipes are usually made of concrete and, of necessity, must be quite large in order to serve a sizeable community. For example, many sewer mains are four feet or more in diameter. Furthermore, as a result of careful planning, a sewer line is seldom full of waste water.

Obviously, in most cases, water cannot forever run down hill. Therefore, pumping stations are strategically located so as to raise the water for another down hill journey until it finally reaches the sewage treatment plant.

Calculating the flow of water, due to gravity, through a sloping pipe that is partically filled with water, is the problem now before us. The formulas used are arrived at empirically, and the dictionary defines empirical as "derived by observation or experiment; guided by practical experience and not theory." This is certainly the case in the following.

The first expression we will use is known as the Chezy formula:

$$V = C\sqrt{R_H S}$$

Where V = velocity in ft./ sec.

C is a coefficient

S is the slope

R_H = hydraulic radius in feet

$$R_H = \frac{\text{cross sectional area}}{\text{wetted perimeter}}$$

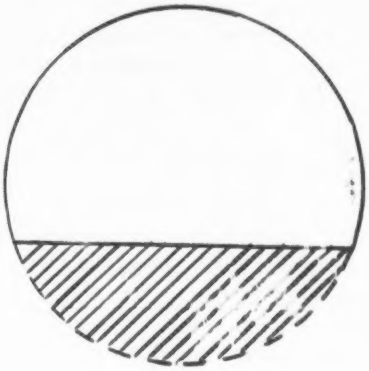
$$C = \frac{1.49(R_H)^{.167}}{n}$$

Where n = 0.15 for concrete pipes.

'n' is about the same for other pipes with smooth internal surfaces.

The cross section of a cylindrical pipe is a circle. If partially filled with water,

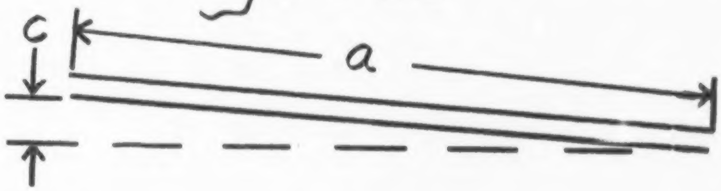
Figure IX



cross sectional area = hatched portion

wetted perimeter = dotted line

Figure X



Slope is defined as $\frac{a}{c} = \frac{\text{length of pipe in feet}}{\text{drop in feet}}$

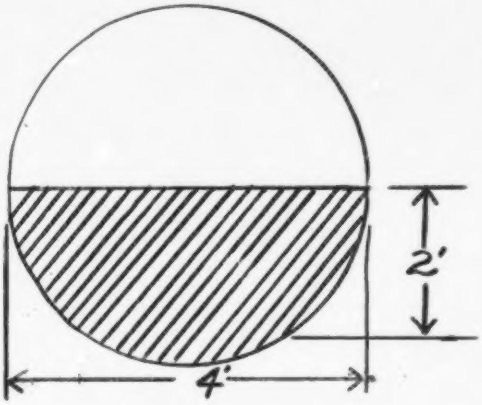
Now let's tackle a relatively easy problem. What is the flow of water through a four foot diameter concrete pipe that is half filled with water; the slope is 0.5 ft. per 100 ft. of pipe?

$$R_H = \frac{\text{cross sectional area}}{\text{wetted perimeter}}$$

$$R_H = \frac{1/2\ \pi\ r^2}{\pi\ r} = \frac{r}{2} = \frac{2}{2} = 1$$

$$C = \frac{1.49(R_H)^{.167}}{n} = \frac{1.49(1)^{.167}}{.015} = 99.33$$

Figure XI



$$\text{Velocity} = C\sqrt{R_H S} = 99.33\sqrt{1 \times \frac{.5}{100}} = 7.02 \text{ ft./sec.}$$

$$\text{Volume} = \text{velocity} \times \text{area} = \text{ft./sec.} \times \text{ft.}^2 = \text{ft.}^3\text{/sec.}$$

$$\text{Volume} = 7.02 \times 1/2\ \pi\ r^2 = 7.02 \times .5 \times 3.14 \times 4$$

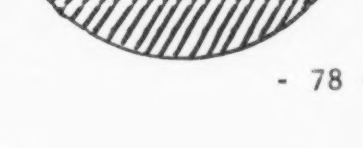
$$\text{Volume} = 44.13 \text{ ft.}^3\text{/sec.}$$

$$\text{Volume} = 44.13 \times 7.48 \times 60 = 19{,}800 \text{ gal./min.}$$

If the pipe is more (or less) than half full, the calculations become more complicated. For example, let us do the above problem keeping everything the same, except the depth of water in the pipe is 1.3 ft.

To do this, we must be able to calculate the area of a segment of a circle and the length of an arc.

Exercise 8



Prove that the area of the hatched area is equal to

$$\text{area} = r^2\left(\frac{\theta}{2} - \sin\frac{\theta}{2}\cos\frac{\theta}{2}\right)$$

Figure XII

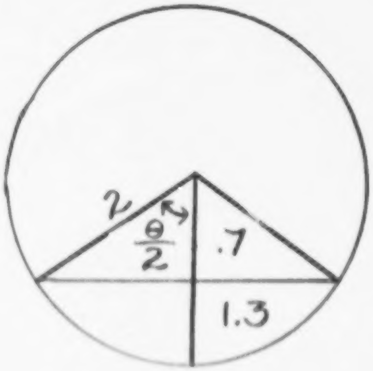
Exercise 9

Prove that in the above sketch, the length of arc is:

$$\frac{180}{3.14 \times r} = \frac{\Theta}{\text{arc}} \quad , \quad \text{arc} = \frac{3.14 \times \Theta \times r}{180}$$

Solution of above problem

Figure XIII



$$\cos\frac{\Theta}{2} = \frac{.7}{2} = .35$$

$$\frac{\Theta}{2} = 69.5^\circ \text{ (from table of natural cosines)}$$

$$\Theta = 139^\circ$$

$\sin 69.5^\circ = .936672$ (from table of natural sins)

$$\text{cross sectional area} = r^2 \left(\frac{\Theta}{2} - \sin\frac{\Theta}{2}\cos\frac{\Theta}{2}\right)$$

$$\text{cross sectional area} = 2^2 \left(\frac{3.14 \times 69.5}{180} - .937 \times .35\right)$$

$$\text{cross sectional area} = 4(1.213 - .328) = 3.54$$

$$\text{wetted perimeter (arc)} = \frac{3.14 \times \Theta \times r}{180}$$

$$\text{wetted perimeter (arc)} = \frac{3.14 \times 139 \times 2}{180} = 4.852$$

$$R_H = \frac{\text{cross sectional area}}{\text{wetted perimeter}}$$

$$R_H = \frac{3.54}{4.852} = .729$$

$$C = \frac{1.49(R_H)^{.167}}{n} = \frac{1.49(.729)^{.167}}{.015} = 94.27$$

$$\text{Velocity} = C\sqrt{R_H S} = 94.27 \times \sqrt{.729 \times \frac{.5}{100}}$$

Velocity = 94.27 x .060 = 5.69 ft./sec.
Volume = 5.69 x 3.54 = 20.15 ft.^3/sec.
Volume = 20.15 x 7.48 x 60 = 9,040 gal./min.

Exercise 10

Calculate the flow in a concrete pipe that is 5 ft. in diameter, slopes .30 ft. per 100 ft. of pipe, and the depth of water in the pipe is 3.8 ft.

Measurement of water flow in open channels

In a pipe, water can be made to flow up hill, or be delivered under pressure to its destination. The foregoing pages briefly discussed, 1) water pressure and 2) flow of water through pipes.

The engineer often handles water in open tanks and channels. To measure the volume of flow in such cases, he uses what is called a "weir". By any other name, a weir is a dam. There are many shapes of weirs, but the ones usually used are either rectangular or triangular in cross section; only these two will be considered here.

To calculate the volume of water flowing over a weir, the height of the water flowing over the weir must be known as well as the size and shape of the weir. There are mathematical formulas which the engineer uses, but all such formulas are empirical; that is, they are tailored to fit a specific situation.

No weir formula can be used with complete confidence unless the conditions of use are substantially duplicated. With these limitations clearly in mind, the following equations are given for rectangular and triangular weirs:

Rectangular Weir

$$Q = 3.33 \times L \times (H)^{3/2} \text{ ft.}^3\text{/sec.}$$

Q = flow in ft.^{3}/sec.

L = length of weir in ft.

H = height of water flowing over the weir in feet

3.33 is a constant determined experimentally for a specific situation. It is sometimes called a "fudge factor".

Exercise 11

Show that the above formula may also be written as:

$$Q = 1495 \times L \times (H)^{3/2} \text{ gal./min.}$$

Using this formula, let us calculate the flow in gallons per minute flowing over a rectangular weir that is 10 ft. long, when the height of water flowing over the weir is .01 ft.

$$Q = 1495 \times 10 \times (.01)^{3/2} = 14.95 \text{ gal./min.}$$

Exercise 12

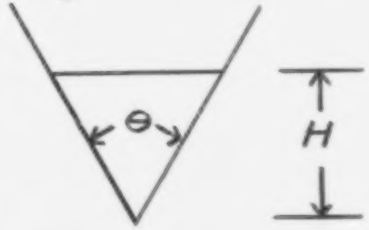
Calculate the flow of water in gal./min. over the above weir when the height of overflow is .1 ft. and 1.0 ft.

Triangular or V-Notch Weir

Obviously, a V-Notch dam will impede the flow of water; thus a given volume of water will have to rise higher in order to pass through the V-shaped opening. Herein is the primary advantage of the V-Notch weir: it permits the engineer to measure more accurately the volume of water being treated by his plant. Also, as noted below, the angle of the V influences the flow of water through a V-Notch weir, which the civil engineer includes in the original design of the plant.

$$Q = 2.56 \tan \frac{\theta}{2} (H)^{5/2} \text{ ft.}^3\text{/sec.}$$

Figure XIV



2.56 is an experimentally determined factor.

θ is the angle of the V-Notch.

H = height of ft. of water above point of V.

Exercise 13

Show that the above formulas become

$$Q = 2.56 (H)^{5/2} \text{ for } 90^\circ \text{ V.}$$
$$Q = 1.478 (H)^{5/2} \text{ for } 60^\circ \text{ V.}$$
$$Q = .686 (H)^{5/2} \text{ for } 30^\circ \text{ V.}$$

Let us calculate the flow of water through a V-Notch weir of 90° when the height of water over the V is 0.3 ft.

$$Q = 2.56\ (.3)^{5/2} = 2.56 \times .0493$$

$$Q = .1262\ \text{ft.}^3/\text{sec.}$$

$$Q = .1262 \times 7.48 \times 60 = 56.6\ \text{gal./min.}$$

Exercise 14

Calculate the flow of water over the above weir in $\text{ft.}^3/\text{sec.}$ and gal./min. when V = 30° and 60°.

In practice, as will be shown in later mini-course, weirs - by any other name - are important components of water purification and waste-water treatment plants. For example, the perimeter of a primary settling tank uses a weir for the overflow of sewage water after the settleable solids have sunk to the bottom of the tank. Such weirs usually have a straight edge which is equivalent to an elongated rectangle; a typical tank is 150 ft. in diameter, and three such tanks handle ninety million gallons of waste-water per day.

Exercise 15

What is the depth of water overflowing the weir of each of the above primary settling tanks?

The final settling basins of a waste-water treatment plant have V-Notch weirs since the sanitary engineer - by law - must carefully record the volume of treated water discharged by his plant. The V-Notch weir, as noted above, provides for such accurate measurements.

Exercise 16

Suppose there are 200 V-Notch weirs in the final settling basin of a waste-water treatment plant, each weir is 90° and the total volume of water is ninety million gallons/day. What is the height of water in each weir?

Weirs are also an important part of a water purification plant. In the mini-course, "The Purification of Water", it will be seen that weirs control the flow of water through large settling tanks, thus permitting the settling of chemically-formed precipitates. These precipitates - called floc - tend to carry with them solid particles that are suspended in the raw water entering the plant.

Stream or River Flow

The sanitary engineer or chemist at a water purification plant often needs to know the quantity of water flowing down a nearby stream or river, which is another example of water flow in open channels. The stream or river may be the source of raw water entering purification plant or the receiving end of a sewage treatment plant. Actually, many rivers perform both functions.

To measure stream or river flow, a site is carefully selected so that the results obtained are reasonably reproducible and thus dependable for future reference. Two situations that meet these requirements are a bridge or dam, both having stable banks. The height of water under the bridge or over the dam is related to the stream flow, the results tabulated, and used forever after.

All this is much easier said than done.

Having selected a good site, the engineer then uses a so-called "current meter." The one most commonly used in the United States by the U.S. Geological Survey is the Price meter. It consists of six conical cups rotating about a vertical axis. Tail vanes keep the meter facing into the current and a heavy weight keeps the supporting cable as nearly vertical as possible. The whole set-up is so heavy that special cranes are usually employed.

The other type of current meter consists of a propeller attached to a horizontal axis. In both cases, the current flow causes the shaft of the meters to rotate.

Current meters are calibrated under conditions of known current flows. One way to do this is to mount the meter on a carriage which is then moved at a known rate over a body of still water. Numerous determinations are made at various speeds and the results plotted.

The rate of flow of water down a stream or river is not the same at different points in its width (horizontally) or at different points of depth (vertically). Thus the stream is divided into a number of points across its width and the velocity determined at two depths for each point. On the basis of many field tests, the variation for most channels is such that the average of the velocities at depths of 20% and 80% of the total depth fairly well equals the average velocity of the stream or river at that point. All of the velocities at each point in the river are then averaged to give the stream velocity. Here, again, the actual procedure used is necessarily abbreviated.

Thus it is that the engineer measures the velocity in ft/sec. of the water flowing down stream of river. He then must determine the cross sectional area of the stream - in square feet - at the point of measurement. The product of these two numbers equals the flow of water in cu. ft./sec. for a given height of water - under the bridge or over the dam. These are plotted and thereafter a measurement at either location tells the story.

For example, the flow of water down the Tennessee River at Chattanooga has been determined by the U.S. Geological Survey with the following results:

Height of River in Feet	Flow in 1000 cu. ft./sec.
6	9
10	23
14	42
18	70
22	97
26	123
30	160
34	190

As previously stated, the purpose of this mini-course is not to compress a degree in engineering into one easy lesson. Therefore, only two more subjects will be considered since water cannot be handled and controlled without them: pumps and valves.

Basically, there are two kinds of pumps: 1) positive pressure and 2) positive displacement. To some extent, at least, this is an over simplification since there are many types of each of these two kinds of pumps.

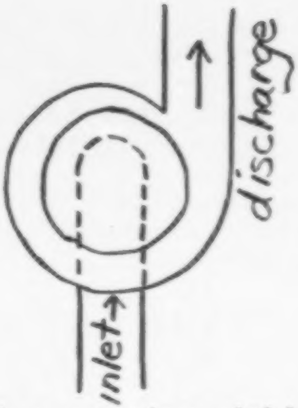
Positive Pressure Pumps

Centrifugal pumps are the positive pressure pumps which are most widely used for moving water from one place to another. They are available inalmost all sizes from a few gallons up to 100,000 gallons/minute. They are made to develop pressures (discharge heads) from a few feet up to several thousand pounds per square inch.

Centrifugal pumps are widely used because they are relatively simple, inexpensive, small in size, easy to maintain and repair, and quiet.

Basically, a centrifugal pump consists of an impeller (or set of blades) rotating withing a tightly fitting circular casing. The shaft to which the blades are attached is driven by a motor of appropriate horsepower, so that the revolving blades produce a reduction in pressure (suction) which draws the water into the entrance opening of the pump. The rotating blades force the water outward with increasing velocity towards and out of the discharged port.

Figure XV



The combination of blades rotating within a housing plus the horsepower delivered to the shaft limits the top pressure which a centrifugal pump can deliver. This is an important characteristic of this type of pump, since it can be (and is) designed to deliver no greater pressure than the overall system can withstand.

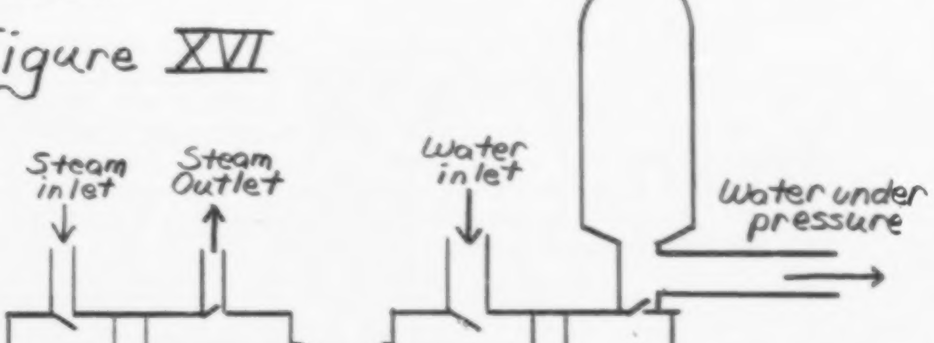
Positive Displacement Pumps

Whereas the pressure developed by a centrifugal pump is determined by the speed of rotation, a positive displacement pump will produce whatever pressure is obtainable by the applied horsepower of the drive motor and/or the strength of the pump parts. If the flow of water is restricted, pressure can be developed sufficient to burst the pump, pipes or other parts of the overall system.

In general, the overall efficiency of positive-displacement pumps is greater than centrifugal pumps. Perhaps for this reason, they are usually used to pump water from a purification plant to a reservoir or elevated tank. In this way, the build-up of excessive pressures is prevented since the system in not closed; the water just rises in the reservoir and/or elevated storage tank. These, in turn - as noted several pages back - maintain a constant pressure in the water system due to their elevation.

Piston pumps are the type of positive displacement pump commonly used by water plants. A piston is often connected directly to a steam cylinder which provides the energy for pumping the water. Valves open and close to control the intake and discharge of water. A schematic sketch of a piston pump is as follows:

Figure XVI



Piston Pump

Pumping Water from Wells

A later mini-course points out that much of the drinking water used in the United States comes from underground wells or streams. In most cases, this water is so pure that it is pumped directly to the user "as is".

Perhaps most students taking this course have had no first-hand experience with the old-fashioned hand pump used down on the farm. But any students having had an introductory course in physics knows that a surface pump draws water from a well by creating a partial vacuum in the pipe leading to the underground water. In other words, it is actually the atmospheric pressure which pushes the water up the pipe. Atmospheric pressure is limited to 34 feet of water.

Exercise 17

Prove that 1 atmosphere pressure is equivalent to 34 feet of water.

The best and most efficient surface pump made can therefore raise water no more than 34 feet. In practice, there are losses that significantly reduce this figure. The hand pump on the farm was probably less than 50% efficient, which means that it was capable of lifting water 17 feet or less.

Thus, for deep wells, pumps must be placed in the underground source of water and force the water to the surface. The only limitation in this case is the capacity of the pump.

Valves

The varieties and complexities of valves used by engineers far exceed the scope of this mini-course.

Again, at the risk of over-simplification, there are two kinds of valves used for handling water:

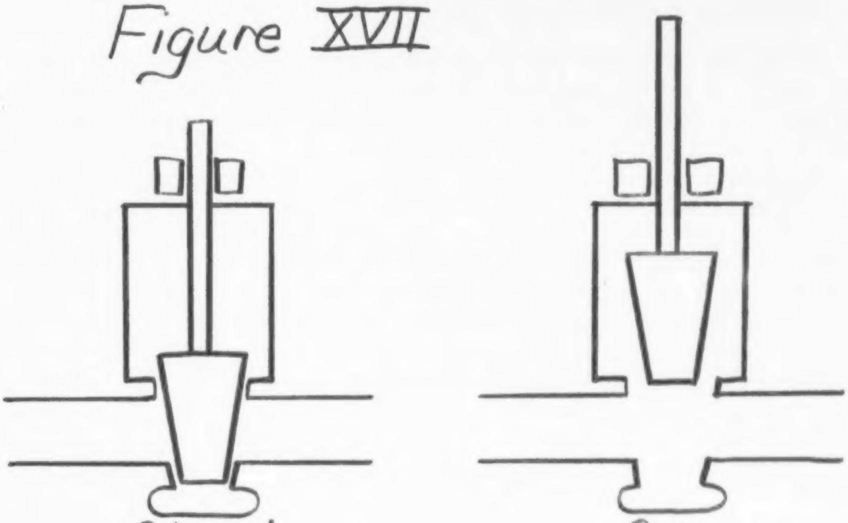
1) Those that are open or shut, thereby allowing the full flow of water or stopping the flow altogether.
2) Those that regulate the amount of flow depending upon the need - such as a faucet in a home.

Gate Valves

Gate valves are typical of those that are used in either the open or shut position since they minimize the pressure drop of water passing through them when the valve is in the open position. When closed, a gate valve effectively stops the flow of water.

The term "gat valve" is almost self-descriptive as the following sketch shows:

Figure XVII



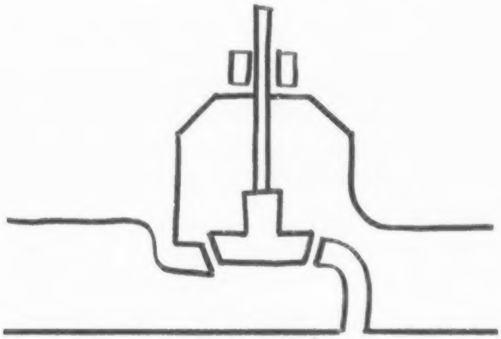
Closed

Open

Globe Valves

This type of valve causes a much greater pressure drop than a gate valve; a globe valve is commonly used to regulate the flow of water. The ordinary home faucet is usually some type of globe valve that looks something like this:

Figure XVIII



Closed

Globe Valve

ANSWERS

A. Pretest

1. 87 lb./in.^{2}
2. 34 feet
3. 1.4 x 10^6 lbs.
4. a) See page 72.
   b) " " 75.
   c) " " 76.
   d) " " 83.
   e) " " 84.
   f) " " 85.
   g) " " 86.
   h) " " 87.
   i) " " 81.
5. 38,600 gal./min.

B. Study Guide

Exercise 1

a) The units of velocity (V) = ft./sec.

Therefore, $V^2 = (\text{ft./sec.})^2$

The units of gravity (g) = ft./sec.^{2}

$$\text{Thus, } \frac{V^2}{g} = \frac{(\text{ft./sec.})^2}{\text{ft./sec.}^2} = \text{ft.}$$

b) The units of pressure (P) = lbs./ft.^{2}

$$\text{The units of density } (\partial) = \frac{\text{lbs.}}{\text{ft.}^3}$$

$$\text{Thus, } \frac{P}{\partial} = \frac{\text{lb./ft.}^2}{\text{lb./ft.}^3} = \text{ft.}$$

Exercise 2

Since there is no flow of water, the terms for kinetic energy drop out of the Bernoulli equation, which then becomes:

$$H_1 + \frac{P_1}{\partial} = H_2 + \frac{P_2}{\partial}$$

$H_2 = 0$, since the faucet is at ground level.

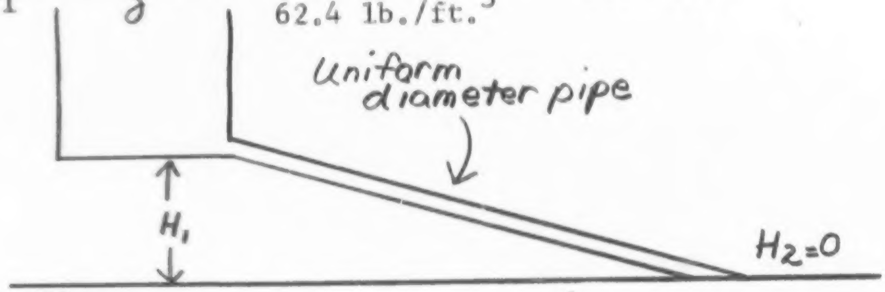
$$H_1 = \frac{P_2 - P_1}{\partial}, \qquad P_2 = 20 \text{ lb./in.}^2$$

$$P_1 = 5 \text{ lb./in.}^2$$

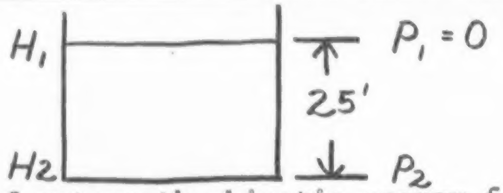
$P_2 - P_1 = 20 - 5 = 15$ lbs./sec.^{2}

$P_2 - P_1 = 15 \times 144 = 2160$ lb./ft.^{2}

$$H_1 = \frac{P_2 - P_1}{\partial} = \frac{2160 \text{ lb./ft.}^2}{62.4 \text{ lb./ft.}^3} = 34.6 \text{ ft.}$$



Exercise 3



There is no flow of water; the kinetic energy factor drops out. The pressure at the top = 0.

Exercise 3 (con.)

$$H_1 + \frac{P_1}{\partial} = H_2 + \frac{P_2}{\partial}$$

$$H_1 - H_2 = \frac{P_2}{\partial}$$

$$25 \text{ ft.} = \frac{P_2}{62.4(\text{lb./ft.}^3)}$$

$$P_2 = \frac{(25 \text{ ft.})(62.4 \text{ lb./ft.}^3)}{144 \text{ in.}^2/\text{ft.}^2}$$

$$P_2 = 11 \text{ lbs./in/}^2$$

Exercise 4

$$F = \frac{W \partial L^2}{2} = \text{ft.} \times \frac{\text{lb.}}{\text{ft.}^3} \times \text{ft.}^2$$

Exercise 5

$$F = \frac{75 \times 62.4 \times (20)^2}{2} = 936{,}000 \text{ lbs.}$$

Exercise 6

1.16 x 7.48 x 60 = 519 gal./min.

Exercise 7

$$d_1 = \frac{1.25}{12}$$

$$A_1 = 3/14 \times {}_{2}\frac{1.25^2}{2 \times 12} = .0085218$$

$$d_2 = \frac{.25}{12}$$

$$A_2 = 3.14 \times \frac{.25^2}{2 \times 12} = .0003408$$

$$P_1 - P_2 = 5$$

$$C = \frac{A_1 \times A_2}{\sqrt{(A_1)^2 - (A_2)^2}} \times \sqrt{2g} = \frac{.0085218 \times .0003408}{\sqrt{(.0085218)^2 - (.0003408)^2}} \times \sqrt{2g}$$

$$C = \frac{.0000029\sqrt{2g}}{\sqrt{.0000726 - .000000}1} = \frac{.0000029}{.0085205} \sqrt{2 \times 32.2}$$

$$C = .0003403 \times 8.02 = .0027$$

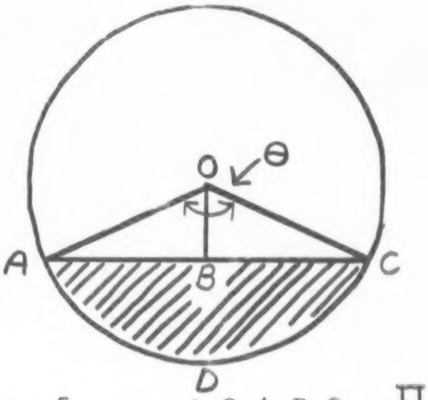
Exercise 7 (con.)

$Q = KC\sqrt{P}$

$Q = .61 \times .0027\sqrt{5} = .00368$ ft.^{3}/sec.

$Q = .00368 \times 7.48 \times 60 = 1.65$ gal./min.

Exercise 8



By definition, the area of a segment of a circle is proportional to the angle of the subtending arc. Thus the area of the segment O A D C is:

$$\frac{\text{Area of segment } O\ A\ D\ C}{\Theta} = \frac{\Pi r^2}{2\Pi}$$

$$\text{Segment} = \frac{\Theta r^2}{2}$$

Area of triangle A O C = A B x O B

$$\sin\frac{\Theta}{2} = \frac{AB}{r}, \quad \cos\frac{\Theta}{2} = \frac{O\ B}{r}$$

$$\text{Area of triangle} = r^2 \times \sin\frac{\Theta}{2} \times \cos\frac{\Theta}{2}$$

Area of hatched area =

area of segment - area of triangle

$$\text{Area of hatched area} = \frac{\Theta r^2}{2} - \left(r^2 \times \sin\frac{\Theta}{2} \times \cos\frac{\Theta}{2}\right)$$

$$\text{Area of hatched area} = r^2\left[\frac{\Theta}{2} - \sin\frac{\Theta}{2} \times \cos\frac{\Theta}{2}\right]$$

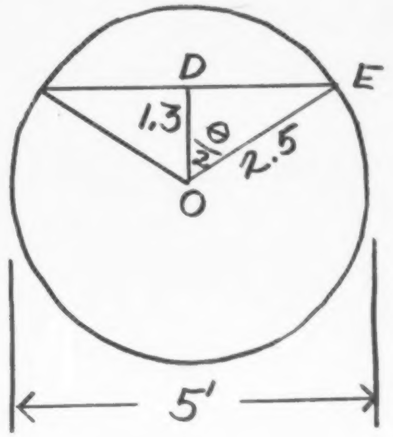
Exercise 9

The length of an arc of a circle is proportional to the angle of the subtending arc.

$$\frac{\text{arc } A\ D\ C}{\Theta} = \frac{\Pi r}{180}$$

$$\text{arc } A\ D\ C = \frac{\Pi \Theta r}{180}$$

Exercise 10



$$\sin \frac{\theta}{2} = \frac{DE}{r}$$

$$\cos \frac{\theta}{2} = \frac{OD}{r}$$

$$DE = r \sin \frac{\theta}{2}$$

$$OD = r \cos \frac{\theta}{2}$$

Area of $\triangle = r^2 \sin \frac{\theta}{2} \cos \frac{\theta}{2}$

$$\cos \frac{\theta}{2} = \frac{1.3}{2.5} = .52$$

$\frac{\theta}{2} = 58^\circ 40' = 58.67^\circ$ (from table)

$\sin 58.67^\circ = .8542$

$$\text{Area} = 1/2\, \Pi\, r^2 + r^2 x \sin \frac{\theta}{2} x \cos \frac{\theta}{2} =$$

$$r^2 \left[\frac{\Pi}{2} + \sin \frac{\theta}{2} \cos \frac{\theta}{2}\right]$$

$$\text{Area} = (2.5)^2 \left[\frac{3.14}{2} + .52 \times .8542\right]$$

Area = 6.25 x 2.01 = 12.56

Total angle = $180^\circ + 2 \times 58.67^\circ = 297.34^\circ$

$$\frac{360}{5 \times \Pi} = \frac{297.34}{\text{arc}}$$

arc = 13.0 feet

$$R_H = \frac{\text{cross sectional area}}{\text{wetted perimeter}} = \frac{12.56}{13.0} = .966$$

$$C = \frac{1.49(R_H)^{.167}}{n} = \frac{1.49(.966)^{.167}}{.015}$$

$$C = \frac{1.49 \times .99}{.015} = 98.77$$

$$\text{Velocity} = C \sqrt{R_H S} = 98.77 \sqrt{.966 \times \frac{.3}{100}}$$

Velocity = $98.77 \sqrt{.0029}$ = 5.32 ft./sec

Volume = 5.32 x 12.56 = 66.78 ft.^{3}/sec.

Volume = 66.78 x 7.48 x 60 = 30,000 gal./min.

Exercise 11

$Q = 3.33\ L\ (H)^{3/2}$ ft.^{3}/sec.

$Q = (3.33 \times 7.48 \times 60) = 1495\ L\ (H)^{3/2}$ gal./min.

Exercise 12

a) $Q = 1495 \times 10 \times (.1)^{3/2} = 1495 \times 10 \times .0316$

$Q = 473$ gal./min.

b) $Q = 1495 \times 10 \times (1)^{3/2} = 1495 \times 10 \times 1$

$Q = 14{,}950$ gal./min.

Exercise 13

a) $\tan \frac{90^\circ}{2} = \tan 45^\circ = 1$

b) $\tan \frac{60^\circ}{2} = \tan 30^\circ = .57735$

$.57735 \times 2.56 = 1.478$

c) $\tan \frac{30^\circ}{2} = \tan 15^\circ = .2679$

$.2679 \times 2.56 = .686$

Exercise 14

a) $Q = .686 \times .0493 = .0338$ ft.^{3}/sec.

$Q = .0338 \times 7.48 \times 60 = 15.2$ gal./min.

$Q = 1.478 \times .0493 = .0729$

$Q = .0729 \times 7.48 \times 60 = 32.7$ gal./min.

Exercise 15

$\pi d = 3.14 \times 160 = 520$ ft. circumference of weir

30 million gal./day/tank =

$\frac{30 \times 10^6}{24 \times 60} = 20{,}833$ gal./min.

$Q = 1495 \times L \times H^{3/2}$

$20{,}833 = 1495 \times 502 \times H^{3/2}$

$H^{3/2} = .0277$ ft.

$\sqrt[2]{H^3} = .0277$

$H^3 = .000767$

$H = .0915$ ft. = 1.1 in. depth of overflow

Exercise 16

$Q = 1.478(H)^{5/2}$ ft.^{3}/sec.

$Q = 2.56 \times 7.48 \times 60(H)^{3/2} = 1149\ (H)^{5/2}$ gal./min.

$\frac{90 \times 10^6}{24 \times 60} = 62{,}500$ gal./min. overflowing all weirs

$\frac{62{,}500}{2{,}000} = 31.25$ gal./min. overflowing each weir

$31.25 = 1149\ (H)^{5/2}$

$(H)^{5/2} = .0272$

$H^5 = .000740$

$H = .236$ ft. = 2.8 in. overflowing each weir

Exercise 17

1 atm = 76 cm mercury

$\frac{76}{2.54} = 29.92$ in. mercury

$29.92 \times 13.6 = 407$ in. water

$\frac{407}{12} = 34$ ft. water

EQUILIBRIUM PRODUCT CONSTANTS

DISSOCIATION CONSTANTS

SUMMARY

Most chemical reactions in the labortory occur rapidly and then appear to stop. When they "stop", we say that the reaction has reached equilibrium. This Study Guide develops a quantitative measure of chemical reactions that reach equilibria, and that "measuring stick" is known as the equilibrium product constant.

ACKNOWLEDGEMENT

The author greatly appreciates the skills of Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College, whose teaching experience is reflected in this Study Guide.

PREREQUISITES

Before tackling this mini-course, the student should be able to handle:

1. Square roots of simple numbers.
2. Square roots of numbers multiplied by powers of ten.
3. Conversion of numbers to logarithms.
4. Conversion of logarithms to numbers.
5. The solution of quadratic equations.
6. The plotting of data in graph form.
7. Titration techniques using volumetric burettes and a pH meter.
8. Use and standardization of a pH meter.
9. Define pH and interconvert between pH and $[H^+]$ or $[OH^-]$ in water solution.

OBJECTIVES

At the end of this mini-course, the student should be able to:

1. State the concept of equilibrium constants and describe how to use them.
2. Use equilibrium constants to calculate the concentration of one of the reactants or products when given the other values.
3. State what is meant by a strong acid and a strong base and identify the common strong acids HCl, HNO_3, and H_2SO_4 and the strong bases NaOH, $Ca(OH)_2$, and KOH.
4. State what is meant by a weak acid and a weak base and identify acetic acid as a weak acid and ammonium hydroxide as a weak base.
5. State what is meant by hydrolysis.
6. Describe the use of a pH meter to perform an acid-base titration and, when given suitable data, plot and determine the end-point of the titration.
7. Use a pH meter to perform an acid-base titration and analyze the data graphically.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. Given the equation: $HX \rightleftharpoons H^+ + X^-$, write the expression for the ionization constant.
2. What is the pH of a 0.02 M solution of the strong acid, HNO_3?
3. A strong base is one which (1) ionizes over 1%, (2) reacts with all acids, (3) reacts with strong acids, (4) ionizes 100%, (5) none of these.
4. One example of a weak acid is (1) HNO_3, (2) H_2SO_4, (3) CH_3COOH, (4) HCl, (5) all of these are weak.
5. What would be the $[OH^-]$, $[H^+]$, and pH of a 0.02 M solution of ammonium hydroxide, NH_4OH? ($K_i = 1.8 \times 10^{-5}$.)
6. The equation: $C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$ is an example of (1) neutralization, (2) combustion, (3) hydrolysis, (4) dissociation, (5) ionization.
7. For the equation in #6, what is the mathematical expression for the equilibrium constant?
8. Given the following data, determine the end-point of the titration by graphical methods.

ml acid -	0	5	10	12	13	14	15	16	17	20
pH -	12.0	11.6	11.2	10.8	10.1	6.8	4.0	3.4	3.1	2.8

I. INTRODUCTION

When one chemical is added to another, a reaction may or may not occur. For present purposes, it is sufficient to know that a reaction will occur in aqueous solutions because of one of several reasons. Let us look at a few examples.

A. Precipitation:

$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNo_3$

$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + BaCl_2$

These two reactions are used frequently. Therefore, they do occur.

Exercise 1

What do these reactions have in common?

B. Oxidation-Reduction:

$Zn^o + 2HCl \rightarrow ZnCl_2 + H_2$

$2H_2O \rightarrow 2H_2 + O_2$

Exercise 2

What do these reactions have in common?

C. Acid Base

$HCl + NaOH \rightarrow NaCl + H_2O + \text{heat}$

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + H_2O + \text{heat}$

Exercise 3

What do these reactions have in common?

Exercise 4

In conclusion, we may say that a reaction will occur in aqueous solutions if:

a. -

b. -

c. -

All chemical reactions eventually reach an end-point; the mere fact that they stop reacting means that the initial reactants have been exhausted to the point that there is no further driving force. This may take an extremely long time, a split second, or any interval in between. The chemists' simplified language for saying this is:

$$\text{Reactants} \rightarrow \text{Products}$$

When no further increase in product occurs, equilibrium has been reached. This state of equilibrium is defined as the state at which opposite reactions take place at the same rate. When this condition is met, the concentrations of reactant and product do not change, although individual molecules do react. Therefore, we can define:

$K = \frac{[\text{Products}]}{[\text{Reactants}]}$, where K is the equilibrium constant and the brackets, [ ], mean concentrations in moles per liter.

Exercise 5

If we are given the following reaction:

$$A + B \rightarrow C + D$$

then K would equal ....?

Since we have defined K as the equilibrium product constant, it means we have multiplied (thus product) the products and divided by the product of the reactants. By convention the amounts, or concentrations, of the reactants and products are expressed in moles per liter.

To signify moles per liter, we use a bracket [ ].

Exercise 6

Rewrite the expression for K using this information:

K =

Every chemical reaction has a definite equilibrium constant which, at a given temperature, does not change.

II. DISSOCIATION CONSTANTS

We are now prepared to apply the above concept to an important type of chemical reaction - the dissociation of chemical compounds. An example of such a dissociation is the ionization of acetic acid, CH_3COOH, in water.

$$CH_3COOH \leftrightarrows H^+ + CH_3COO^-$$

Exercise 7

Write the K for this dissociation.

Experimentally it was found that an 0.5 M solution of acetic acid has a pH = 2.50.

Exercise 8

How do we express pH mathematically?

Exercise 9

Recall that $[H^+]$ = hydrogen ion concentration in moles per liter. What is the $[H^+]$ for a pH = 2.50?

Exercise 10

If X = $[H^+]$ formed, then what would be the $[CH_3COO^-]$?

Exercise 11

What would be the concentration of the CH_3COOH left undissociated?

Exercise 12

If, as you calculated, X = $[H^+] = [CH_3COO^-] = 3.16 \times 10^{-3}$, what is the value of K?

At 25°C a solution of acetic acid always has a dissociation constant of 1.8×10^{-5}. Knowing this, the $[H^+]$ can be calculated at any other molarity. For example, what is the $[H^+]$ of a 0.001 M solution of acetic acid?

Exercise 13

What will you let equal $[H^+]$ at equilibrium?

Exercise 14

What is $[CH_3COO^-]$ at equilibrium?

Exercise 15

What is $[CH_3COOH]$ at equilibrium?

Exercise 16

What is the value of K for CH_3COOH at 25°C?

Exercise 17

Set up the equilibrium constant expression using these data.

Notice that if you solve this problem you will end up with a quadratic equation. Since 1.8×10^{-5} is a very small number, we know that very little CH_3COOH will dissociate and the concentration of H^+, or X, is very small. Indeed, X is so small compared to 0.001 that it can be dropped without seriously affecting the result. (NOTE: a small number only may be dropped if it is added or subtracted from a large number).

Exercise 18

Rewrite the equilibrium constant expression in Exercise 17 using this approximation.

Exercise 19

Solve the problem for X.

Exercise 20

Calculate the pH.

NOTE: If the equation had been solved as a quadratic equation then $X = 1.25 \times 10^{-4}$. This is an error that can be tolerated, but for more dilute solutions it would be necessary to use the quadratic equation.

Exercise 21

It is now time for you to solve a complete problem. An 0.35 M solution of CH_3COOH would have what pH?

The calculations above enable us to get a quantitative idea of what is meant by a weak acid. Weak acids are those which are not completely ionized in water.

For a 0.5 M solution of acetic acid, the

$[H^+] = 3.16 \times 10^{-3} = 0.00136$. Therefore:

$$\frac{0.00136}{0.5} \times 100 = 0.63\%\ H^+$$

Or 99.37% CH_3COOH remains unionized!

Some of the more frequently used dissociation constants are listed in Table III.

Strong acids such as H_2SO_4, HCl, and HNO_3, and most salts are completely ionized in aqueous solutions.

Weak bases are also slightly ionized; that is why they, too, are weak. For example, the dissociation constant of NH_4OH is 1.8×10^{-5}:

$$NH_4OH \rightarrow NH_4^+ + OH^-$$

Exercise 22

What would be the expression for K?

Exercise 23

Recall that $[H^+][OH^-] = 1 \times 10^{-14}$. What, then, is the pH of a 0.5 M solution of NH_4OH? Let $X = [OH^-]$.

The dissociation constants of some weak bases are also listed in Table III. Strong bases such as NaOH and KOH are completely ionized in aqueous solutions.

III. POLY-ACIDS AND POLY-BASES

Many acids have more than one hydrogen in the molecule that can become an H^+ ion; many bases contain more than one OH^-. Some texts refer to these as poly-acidic acids and poly-basic bases.

Since strong acids and bases are completely ionized in water, it makes no difference whether it is a mono-acidic acid (HCl) or a di-acidic acid (H_2SO_4), both release all their hydrogens as H^+ - so far as we can determine.

It is quite different with weak poly-acids and weak poly-bases. A classic example is phosphoric acid - H_3PO_4. When this poly-acidic acid is dissolved in water it ionizes as follows:

(1) $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$

(2) $H_2PO_4^- \longrightarrow H^+ + HPO_4^{--}$

(3) $HPO_4^{--} \longrightarrow H^+ + PO_4^{---}$

K_1 (first dissociation constant) $= 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$

K_2 (second dissociation constant) $= 6.2 \times 10^{-8} = \frac{[H^+][HPO_4^{--}]}{[H_2PO_4^-]}$

K_3 (third dissociation constant) $= 4.8 \times 10^{-13} = \frac{[H^+][PO_4^{-3}]}{[HPO_4^{-2}]}$

Exercise 24

a. 1. Express K_1 in terms of concentrations.

2. Repeat for K_2.

3. Repeat for K_3.

b. Use K_1 (only) to calculate the pH of a 0.5 M solution of H_3PO_4.

Suppose that enough KOH has been added to a liter of 0.5 H_3PO_4 to neutralize one of the H^+ ions.

Exercise 25

This reaction would give: $H_3PO_4 + KOH \longrightarrow ?$

As previously stated, all salts are completely ionized in water so that KH_2PO_4 goes completely to $K^+ + H_2PO_4^-$. Our interest now rests on the $H_2PO_4^-$ which ionizes as previously indicated.

Exercise 26

For a 0.5 M solution, what would be the pH if we did neutralize the first H^+? (Assume that only K_2 is important).

Exercise 27

Calculate the pH if we had neutralized the first two H^+ in H_3PO_4 so that we would be looking at the following reaction:

$$HPO_4^{--} \longrightarrow H^+ + PO_4^{---}$$

Summarizing the above calculations, a 0.5 M solution of H_3PO_4 should react with a base in three steps, in effect, it is three acids:

(1) $H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ pH = 1.24 a strong acid

(2) $H_2PO_4^- \rightarrow H^+ + HPO_4^{--}$ pH = 3.76 a fairly weak acid

(3) $HPO_4^{--} \rightarrow H^+ + PO_4^{---}$ pH = 6.81 practically that of water

Neutralizing a 0.5 solution of H_3PO_4, with a strong base, results in the following data and gives an interesting titration curve.

TABLE I

pH	KOH ml	pH	KOH ml	pH	KOH ml
1.79	0.0ml	6.30	17.0ml	7.88	27.0ml
2.10	5.0	6.49	18.0	8.69	28.0
2.30	7.0	6.60	19.0	10.40	29.0
2.49	9.0	6.71	20.0	10.80	30.0
2.60	10.0	6.81	21.0	11.15	32.0
2.75	11.0	6.95	22.0	11.49	35.0
2.98	12.0	7.00	22.4	11.65	37.5
3.21	13.0	7.09	23.0	11.80	40.0
4.80	14.0	7.21	24.0	12.05	45.0
5.79	15.0	7.39	25.0	12.21	50.0
6.10	16.0	7.59	26.0		

Exercise 28

Using rectangular graph paper, plot pH as the ordinate and ml. KOH added as the abscissa.

Exercise 29

Explain the shape of the curve.

The classic example of a weak poly-basic base is Na_2CO_3; this does not appear to be a base since it contains no H^+ or OH^- in its chemical structure. Yet a 0.5 M solution of Na_2CO_3 has a pH = 12.0 which means that it is fairly basic. Why?

Exercise 30

Can you state why some salts, such as Na_2CO_3, are basic?

Exercise 31

Using NaCl as an example, explain why many salts are neutral when in aqueous solution.

Exercise 32

Try to use an equation to explain why the pH of a Na_2CO_3 solution isn't neutral.

Since, experimentally, a 0.5 M solution of Na_2CO_3 is basic, what is the source of the OH^-? The source is, and can only be, water. The reaction of such a salt with water is known as hydrolysis.

$$Na_2CO_3 + H_2O \longrightarrow NaOH + NaOH_3$$

Cancelling the Na^+ common to both sides of the equation, the above becomes

$$CO_3^{--} + H_2O \rightarrow OH^- + HCO_3^-$$

$$K_1 = \frac{[OH^-][HCO_3^-]}{[CO_3^{--}]} = 2.1 \times 10^{-4}$$

Note that H_2O is not included in the mathematical expression. Water is the solvent as well as a reactant, so we give it a defined "concentration" of unity. Therefore, the solvent will not be shown in the equilibrium expression even if it is a reactant as well.

Three points of equilibria can be recognized, their pH calculated from the equilibrium constants, and these compared to the experimental results.

First point = initial solution of Na_2CO_3.

Let x = the amount of CO_3^{--} which reacts with water

then x also equals the amount of OH^- and there must also be a HCO_3^- for each OH^-. Substitute these facts in the above equation.

Exercise 33

What is the $[OH^-]$?

Exercise 34

What is the pH?

Experimentally, the initial pH = 11.3 instead of 12.0. Such differences are expected with fairly concentrated solutions since these calculations assume no ionic attractions. This assumption is good in dilute solutions, but becomes less accurate at concentrations above 0.1 M.

A 0.5 M solution of Na_2CO_3 was neutralized with a solution of H_2SO_4, the results are given below:

TABLE II

pH	H_2SO_4 ml	pH	H_2SO_4 ml	pH	H_2SO_4 ml
11.30	0	9.52	18.0	7.30	26.4
10.50	5	9.45	19.0	7.20	27.0
10.35	7	9.35	20.0	7.05	28.0
10.19	9	9.20	21.0	7.00	28.4
10.10	10	9.05	22.0	6.82	30.0
9.99	12	8.90	23.0	6.40	35.0
9.85	14	8.45	24.0	6.05	40.0
9.78	15	7.70	25.0	5.60	45.0
9.60	17	7.40	26.0	3.10	50.0

Exercise 35

Plot the results from Table II. (Use graph paper.)

Exercise 36

At what volume did the center of the first break in the curve occur?

This is the point where the OH^- in the above equation has been neutralized by the H^+ of the strong acid. Therefore, at the halfway mark of this first step - that is when 12.25 ml of H_2SO_4 have been added - half of the CO_3^{--} have been converted to HCO_3^-, so this represents the second equilibrium which can be recognized and at this point:

$$[CO_3^{--}] = [HCO_3^-]$$

$$2.1 \times 10^{-4} = K_1 = \frac{[HCO_3^-][OH^-]}{[CO_3^{--}]} = [OH^-]$$

(since $[CO_3^{--}] = [HCO_3^-]$)

$$[H^+] = \frac{Kw}{[OH^-]} = \frac{1 \times 10^{-14}}{2.1 \times 10^{-4}} = 4.8 \times 10^{-11}$$

$$pH = 10.32$$

The experimental result after the addition of 12.25 ml of H_2SO_4 was pH = 10.0, which again is reasonably good aggreement.

The equilibrium constant and equation for the second step is:

$NaHCO_3 + H_2O \longrightarrow H_2CO_3 + NaOH$ - again cancelling out Na we have:

$$HCO_3^- + H_2O \longrightarrow H_2CO_3 + OH^-$$

K_2 for this reaction = 2.3×10^{-8}

Exercise 37

What is the equilibrium expression for this reaction?

$$K_2 = 2.3 \times 10^{-8} = ?$$

Exercise 38

The second OH^- was neutralized after the addition of what volume of H_2SO_4?

Exercise 39

The halfway mark between these two breaks in the curve therefore occurs at the point where what volume of H_2SO_4 was added?

at this point $[H_2CO_3] = [HCO_3^-]$ and

$$K_2 = 2.3 \times 10^{-8} = \frac{[H_2CO_3]\,[OH^-]}{[HCO_3^-]}$$

Exercise 40

Solve for $[OH^-]$.

Exercise 41

What is the pH?

The dissociation constants of some weak acids at 25°C are given in Table III.

TABLE III

Dissociation constants of some weak acids at 25°C.

Acid	Formula	Dissociation Constant
Acetic	CH_3COOH	$1.75\text{x}10^{-5}$
Benzoic	C_6H_5COOH	$6.3\text{x}10^{-5}$
Boric	H_3BO_3	$6.4\text{x}10^{-10}$
Carbonic	H_2CO_3	$3.5\text{x}10^{-7}$
Chloracetic	$CH_2ClCOOH$	$1.4\text{x}10^{-3}$
Formic	$HCOOH$	$1.76\text{x}10^{-4}$
Hydrocyanic	HCN	$7.2\text{x}10^{-10}$
Oxalic	$(COOH)_2$	$6.5\text{x}10^{-2}$

Dissociation constants of some weak bases at 25°C.

Base	Formula	Dissociation Constant
Ammonium hydroxide	NH_4OH	$1.8\text{x}10^{-5}$
Magnesium hydroxide	$Mg(OH)_2$	$1.2\text{x}10^{-11}$
Calcium hydroxide	$Ca(OH)_2$	$3.5\text{x}10^{-2}$ (K_2)
Zinc hydroxide	$Zn(OH)_2$	$1.5\text{x}10^{-9}$ (K_2)
Sodium carbonate	Na_2CO_3	$2.1\text{x}10^{-4}$ (K_1)
		$2.3\text{x}10^{-8}$ (K_2)

Exercise 42

Given a 0.5 M solution of sodium benzoate, C_6H_5COONa, what is the pH of this solution? The hydrolysis equations are:

$$C_6H_5COO\ Na \longrightarrow Na^+\ C_6H_5COO^-$$

$$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$$

$$\text{K for } \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]} = 1.5 \times 10^{-10}$$

ANSWERS

A. Pretest

1. $K = \frac{[H^+][X^-]}{[HX]}$

2. $[H^+] = 2 \times 10^{-2}$, pH = 1.7

3. (4)

4. (3)

5. $[OH^-] = 6 \times 10^{-4}$, $[H^+] = 1.5 \times 10^{-11}$, pH = 10.8

6. (3)

7. $K = \frac{[C_6H_5COOH]\,[OH^-]}{[C_6H_5COO^-]}$

8. 13.8 ml.

B. Study Guide

1. Each reaction produces a precipitate.
2. They both undergo a change in valence.

$$Zn^{o} \rightarrow Zn^{++}$$
$$H^{+} \rightarrow H_2^{o}$$

3. They are both reactions of an acid with a base and they both liberate heat.

NOTE: Acid-base reactions will always liberate heat.

4. A. A precipitate is formed.
   B. There is a change in valence.
   C. Heat is liberated.
5. You may have answered this question in one of two ways.
   A. $K = \frac{C + D}{A + B}$ or B. $K = \frac{(C)\ (D)}{(A)\ (B)}$

   B is correct.
6. $K = \frac{[C]\ [D]}{[A]\ [B]}$
7. $K = \frac{[H^{+}]\ [CH_3COO^{-}]}{[CH_3COOH]}$
8. $pH = -\log\ [H^{+}]$
9. $\log [H^{+}] = -2.50 = -3.00 + 0.50$

   $[H^{+}] = 3.16 \times 10^{-3}$
10. Since for every CH_3COOH that dissociates an equal number of H^{+} and CH_3COO^{-} are formed, thus if $[H^{+}] = X$ then $[CH_3COO^{-}]$ also = X.
11. $[CH_3COOH]$ = original concentration - concentration lost

    0.5 = original concentration of CH_3COOH

    $[CH_3COOH] = 0.50 - X$ = concentration at equilibrium
12. $K = \frac{[H^{+}]\ [CH_3COO^{-}]}{[CH_3COOH]} = \frac{[X]\ [X]}{[0.5 - X]} = \frac{X^2}{[0.5 - X]}$

    or $K = \frac{[3.16 \times 10^{-3}]^2}{0.5 - 0.00316} = 2.0 \times 10^{-5}$
13. Let $[H^{+}] = X$
14. $[CH_3COO^{-}] = X$
15. $[CH_3COOH] = 0.001 - X$
16. $K = 1.8 \times 10^{-5}$
17. $K = 1.8 \times 10^{-5} = \frac{X^2}{(0.001 - X)}$
18. $1.8 \times 10^{-5} = \frac{X^2}{(0.001)}$

19. $X^2 = 1.8 \times 10^{-5}\ (0.001)$

$X^2 = 1.8 \times 10^{-5}\ (1 \times 10^{-3})$

$X^2 = 1.8 \times 10^{-8}$

$X = 1.3 \times 10^{-4}$

$[H^+] = 1.3 \times 10^{-4}$

20. $pH = -\log 1.3 \times 10^{-4}$

$pH = -(-4.00 + 0.136)$

$pH = 3.86$

21. $K = 1.8 \times 10^{-5}\ \frac{(X)(X)}{(0.35 - X)}$

X is small because K is small

therefore $1.8 \times 10^{-5} = \frac{X^2}{.35}$

$X^2 = 3.5 \times 10^{-1}\ [1.8 \times 10^{-5}]$

$X^2 = 6.30 \times 10^{-6}$

$X = 2.5 \times 10^{-3}$

$pH = -\log 2.5 \times 10^{-3}$

$pH = -(-3 + .4)$

$pH = 2.60$

22. $K = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$

23. $K = 1.8 \times 10^{-5} = \frac{[X][X]}{[0.5 - X]}$ Using the same logic as used with weak acids

$X^2 = 1.8 \times 10^{-5}\ (0.5)$

$X^2 = 0.9 \times 10^{-5} = 9 \times 10^{-6}$

$X = OH^- = 3 \times 10^{-3}$

$[H^+][OH^-] = 1 \times 10^{-14}$

$[H^+] = \frac{1 \times 10^{-14}}{3 \times 10^{-3}}$

$[H^+] = 3.33 \times 10^{-12}$

$pH = -\log [H^+] = -\log 3.33 \times 10^{-12}$

$pH = -(-12 + 0.52) = 11.48$

24. $\frac{X^2}{0.5 - X} = 7.5 \times 10^{-3}$

$X^2 = 3.75 \times 10^{-3}$ (Assuming that $0.5 - X = 0.5$)

$X = [H^+] = 6.13 \times 10^{-2}$

$pH = -\log 6.13 \times 10^{-2}$

$pH = -(-2 + .79)$

$pH = 1.21$

NOTE: Solving the above as a quadratic equation, $X = [H^+] = 5.75 \times 10^{-2}$ and $pH = 1.24$.

25. $KH_2PO_4 + H_2O$

We have neutralized the first proton.

26. $K_2 = \frac{[H^+][HPO_4^{=}]}{[H_2PO_4]} = 6.2 \times 10^{-8}$

$6.2 \times 10^{-8} = \frac{X^2}{[0.5 - X]}$

$X^2 = 3.1 \times 10^{-8}$

$X = 1.74 \times 10^{-4}$

$pH = 3.76$

27. $K_3 = \frac{[H^+][PO_4^{---}]}{[HPO_4^{--}]} = 4.8 \times 10^{-13}$

$4.8 \times 10^{-13} = \frac{X^2}{[0.5 - X]}$

$2.4 \times 10^{-13} = X^2$

$X^2 = 24 \times 10^{-14}$

$X = [H^+] = 4.9 \times 10^{-7}$

$pH = 6.31$

28. Graph shown on separate page. (See page 114-A).

29. It was found that the initial solution had a pH = 1.79 and not 1.24. This difference is to be expected since the activity of the ion is less in concentrated solutions than its concentration - a matter that will be covered later. As the H^+ of the strong acid were neutralized with the KOH there was a gradual rise in the pH until the pH = 3.76, which completed step 1. The addition of more KOH caused a sharp jump to pH = 5.75, which begins step 2; that is, the ionization and neutralization of the second H^+ - which is that of a weak acid. The ionization of the third H^+ has a pH

so nearly that of water that it cannot be distinguished from that of water. The sharp rise at pH = 8.0 shows that all of the H^+ of step 3 have been neutralized and further addition of KOH merely builds up a high pH due to the pressence of OH^-.

30. A salt is the reaction product of an acid and a base. Salts formed by a strong base and strong acid are neutral: their aqueous solutions are neither acidic or basic.

31. $HCl + NaOH \longrightarrow NaCl + HOH$

NaCl is the reaction product of a strong acid HCl and strong base NaOH; therefore, an aqueous solution of NaCl is neutral.

32. $2NaOH + H_2CO_3 \longrightarrow Na_2CO_3 + H_2O$

NaOH is a strong base and carbonic acid is a weak acid, therefore, the final solution is basic.

33. $\frac{X^2}{0.5 - X} = 2.1 \times 10^{-4}$

$X^2 = 1.0 \times 10^{-4}$

$X = 1 \times 10^{-2} = [OH^-]$

34. $[H^+][OH^-] = 1 \times 10^{-14}$

$[H^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12}$

35. Graph shown on separate page. (See page 114-B).

36. 24.5 ml of H_2SO_4 added.

37. $K_2 = 2.3 \times 10^{-8} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$ Remember, H_2O is the solvent and its concentration remains constant.

38. 48 ml

39. 36 ml

40. 2.3×10^{-8}

41. $[H^+] = \frac{1 \times 10^{-14}}{2.3 \times 10^{-8}} = 4.3 \times 10^{-7}$

$pH = -\log H^+ = -\log 4.3 \times 10^{-7} = -(-7 + .6)$

$pH = 6.4$

42. Let $X = [OH^-] = [C_6H_5COOH]$; and $[C_6H_5COO^-] = [0.5 - X]$

$1.5 \times 10^{-10} = \frac{X^2}{0.5 - X}$

42. (continued)

$$X^2 = 0.75 \times 10^{-10}$$

$$X^2 = 75 \times 10^{-12}$$

$$X = 8.6 \times 10^{-6}$$

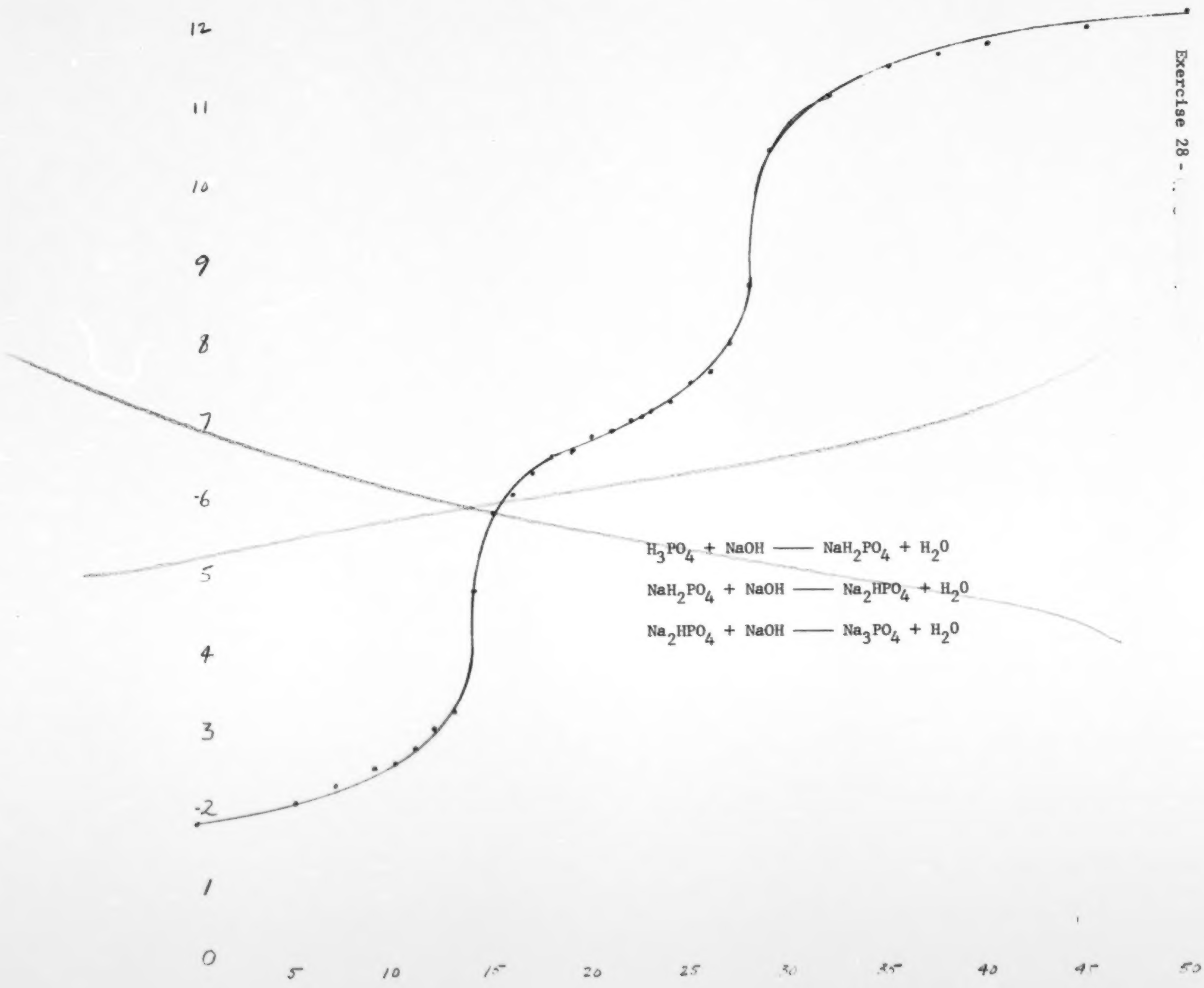
$$[OH^-] = 8.6 \times 10^{-6}$$

$$[H^+] = \frac{1 \times 10^{-14}}{8.6 \times 10^{-6}} = 1.1 \times 10^{-9}$$

$$pH = -\log 1.1 \times 10^{-9}$$

$$pH = -(-9 + .04)$$

$$pH = 8.96$$

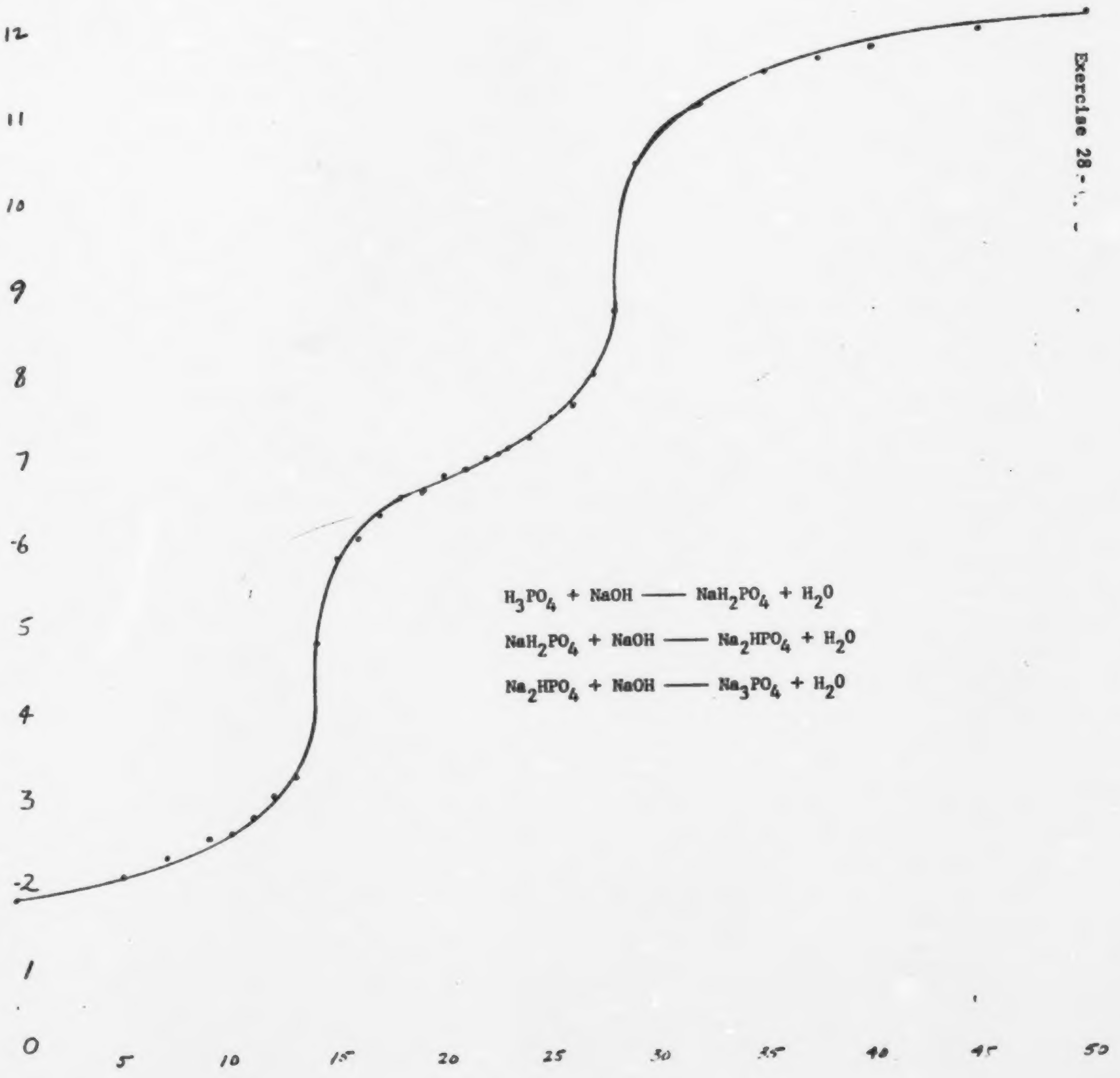


H_3PO_4 + NaOH —— NaH_2PO_4 + H_2O

NaH_2PO_4 + NaOH —— Na_2HPO_4 + H_2O

Na_2HPO_4 + NaOH —— Na_3PO_4 + H_2O

Exercise 28 - [illegible]

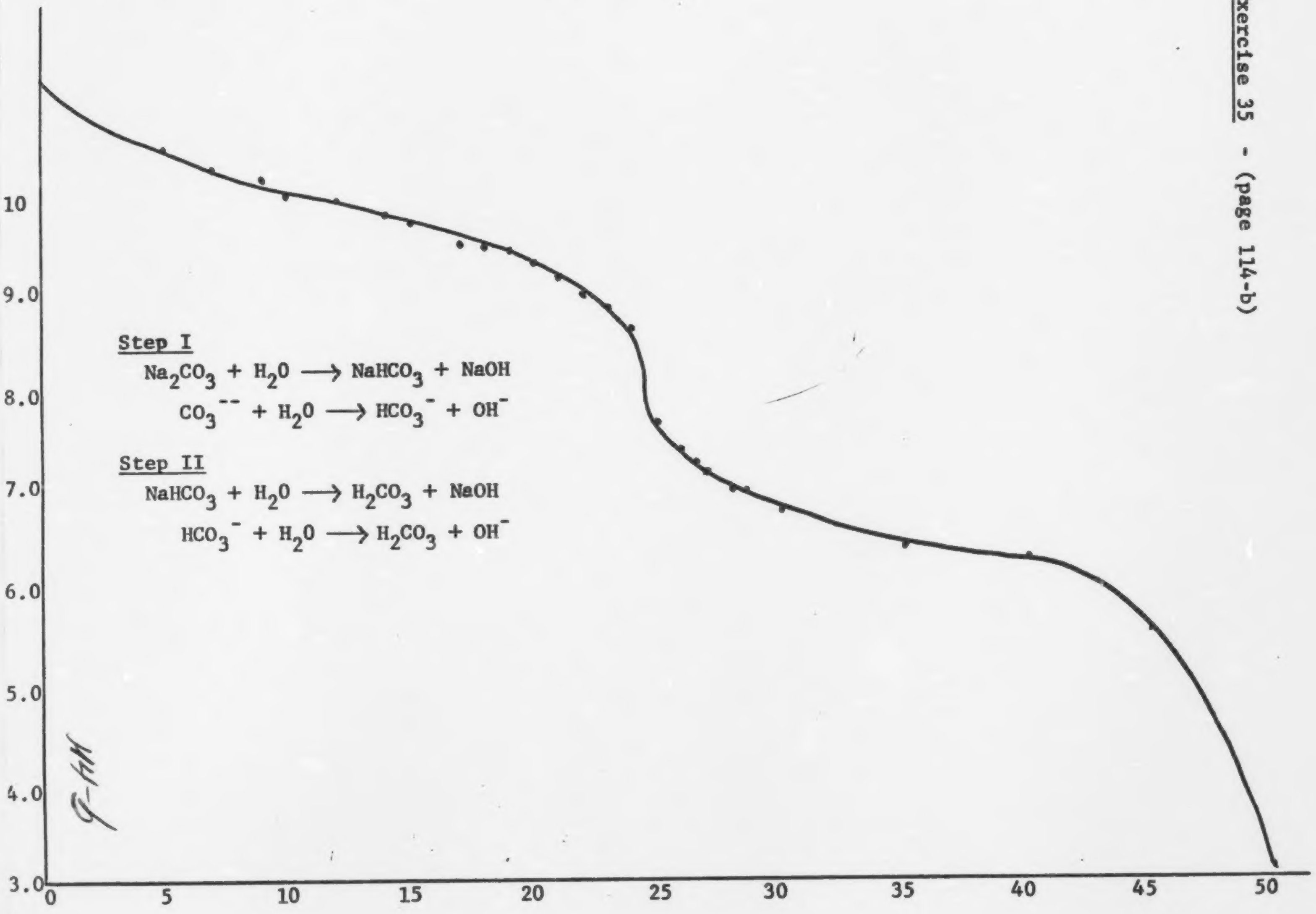


$H_3PO_4 + NaOH \text{ —— } NaH_2PO_4 + H_2O$

$NaH_2PO_4 + NaOH \text{ —— } Na_2HPO_4 + H_2O$

$Na_2HPO_4 + NaOH \text{ —— } Na_3PO_4 + H_2O$

Exercise 35 - (page 114-b)



Step I

$Na_2CO_3 + H_2O \longrightarrow NaHCO_3 + NaOH$

$CO_3^{--} + H_2O \longrightarrow HCO_3^{-} + OH^{-}$

Step II

$NaHCO_3 + H_2O \longrightarrow H_2CO_3 + NaOH$

$HCO_3^{-} + H_2O \longrightarrow H_2CO_3 + OH^{-}$

114-b

EQUILIBRIUM CONSTANTS

SOLUBILITY PRODUCT CONSTANTS

SUMMARY

The concept of solubility and solubility product constants are introduced and related to the equilibrium constants already studied. Conversions from concentration terms to solubility product constants and the reverse are discussed.

RATIONALE

The solubility of insoluble compounds - which isn't as contradictory as it sounds - is an important part of water chemistry. For all practical purposes there is no such thing as "pure" water; all good drinking water contains some dissolved compounds - some of which are desirable and others that should be removed. This Study Guide lays the foundation for the chemist's approach to handling this important part of his duties.

ACKNOWLEDGEMENT

Thanks are due Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College, for helping to change the original manuscript into the following format.

PREREQUISITES

Before beginning this mini-course, the student should be able to:

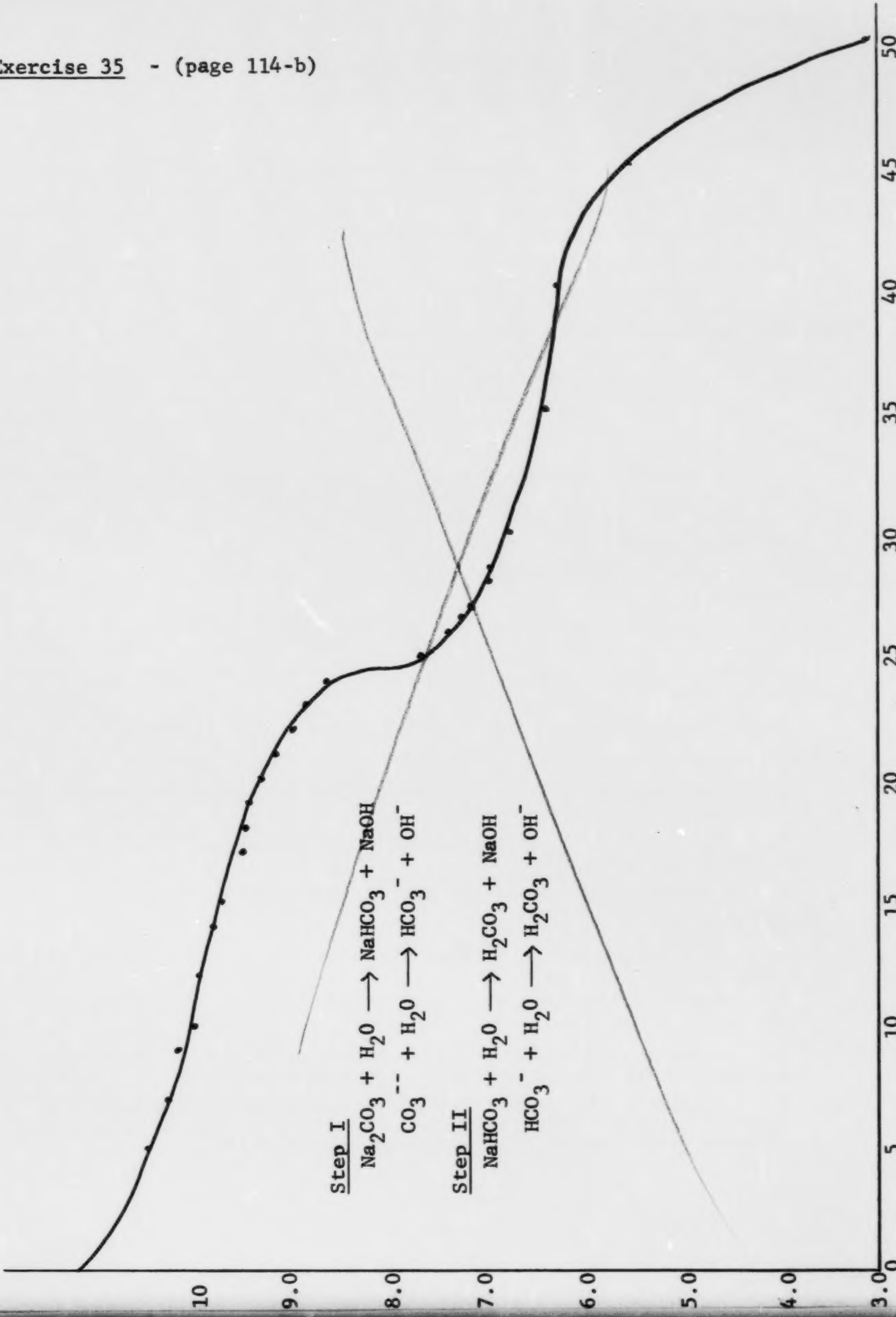
1. Write ionization product constant expressions and use values of K_i to calculate the concentrations of reactants and/or products.
2. State what is meant by solubility, and that nothing is truly insoluble.
3. Use logarithms (some help is given in the answers).
4. Take the square root and cube root of a number.
5. Take the nth root of any number using logarithms (again some help is given in the answers).
6. Use the pH and $[H^+]$ is solving problems and interconvert between pH, $[H^+]$, and $[OH^-]$.
7. Convert from ppm to g/l and to moles/liter.

OBJECTIVES

At the completion of this mini-course, the student should be able to:

1. Describe the effect of solubility of an acid or base upon the pH of a solution.
2. Given a slightly soluble compound, give the mathematical expression for the solubility product constant.
3. Calculate the solubility product constant for a slightly soluble compound when given the solubility in ppm or mole/liter or when given the pH of a slightly soluble base.

Exercise 35 - (page 114-b)



Step I

$Na_2CO_3 + H_2O \longrightarrow NaHCO_3 + NaOH$

$CO_3^{--} + H_2O \longrightarrow HCO_3^- + OH^-$

Step II

$NaHCO_3 + H_2O \longrightarrow H_2CO_3 + NaOH$

$HCO_3^- + H_2O \longrightarrow H_2CO_3 + OH^-$

4. Calculate the pH of a saturated solution of a weak base when given the solubility product constant of that base.

5. Given Ki and the concentration of one ion, calculate the maximum concentration of the other ion which can possibly be dissolved in that solution.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. What would be the pH of a .004 M solution of $Ca(OH)_2$?

2. Given the equilibrium, $Mg(OH)_2(s) \rightleftharpoons Mg^{++} + 2\ OH^-$, correctly express the solubility product constant.

3. Given Ki = 9×10^{-12} for the reaction in #2, what will be the pH of a saturated solution of this base?

4. What will be the solubility of $BaSO_4$ in (a) mole/l and in (b) ppm, if this salt has a solubility product constant of 1.5×10^{-9}?

5. The solubility of AgCl is 2.0 ppm. Calculate the solubility product constant.

6. What is the maximum concentration of Ca^{++} which can be dissolved in a solution containing 0.02 M CO_3^{-2}? K for $CaCO_3$ is 4.7×10^{-9}.

7. When a slightly soluble base is added to water, what happens to the pH? (1) no change, (2) decreases, (3) increases.

8. The pH of a saturated solution of $Zn(OH)_2$ is 8.60. Calculate the solubility product constant.

I. INTRODUCTION

As previously stated, one driving force for a chemical reaction in aqueous solutions is the formation of a precipitate. In such cases, a water insoluble product results when the aqueous solutions of two water soluble compounds are mixed together. Actually, so-called insoluble substances are slightly soluble in water - sea water contains trace amounts of almost everything. Knowing how to calculate aqueous solubility of insoluble compounds - which certainly seems to be a contradictory statement, but isn't - is very important to the water chemist.

For all practical purposes, there is no such thing as "pure" water. Distilled water is quite tasteless and impossibly expensive for general use. Good drinking water always contains a certain amount of dissolved salts, many of which are desirable. Others must be removed in order for the water to be satisfactory for home and industrial use. The understanding of ionization product constants provides a quantitative handle for dealing with this problem.

The chemistry student knows that the following reaction produces a precipitate:

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$

Suppose pure AgCl is placed in a vessel containing 1 liter of distilled water agitated for half an hour or more at 25°C; the aqueous phase is then filtered to remove any trace of the insoluble AgCl; finally the liter of clear filtrate is evaporated to dryness in a tared beaker. It will be found that the new weight of solid remaining equals 0.0025 g. of AgCl, which equals 1.75×10^{-5} moles/liter. Obviously this amount of AgCl was soluble in 1 liter of distilled water at 25°C under conditions of equilibrium. Thus:

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

Exercise 1

What is the ionization product for this reaction?

Since the AgCl is a solid, it is not a part of the solution. Therefore the "concentration" (or activity) of a solid is defined as unity. Thus it is chemically and mathematically proper to drop the AgCl in the denominator of the above equation

Exercise 2

What is the new ionization product for this reaction? This is sometimes called the solubility product constant.

Let X be the moles per liter of AgCl that dissolved to form Ag^+ and Cl^-.

Exercise 3

What is the value of K_i?

This value of K_i for AgCl at 25°C will always be obeyed in saturated solutions. If we increase or decrease the ion content of either the Ag^+ of Cl^-, the other will have to change to maintain $K_i = 3.0 \times 10^{-10}$ at equilibrium. For example, sea-water has a Cl^- content of 16,200 ppm.

Exercise 4

16,200 ppm equals how many g/l?

Exercise 5

16,200 ppm equals how many moles per liter?

Exercise 6

If sea-water contains 0.46 moles/liter of Cl^-, what would be the maximum $[Ag^+]$ in sea water in moles per liter?

Exercise 7

What would be the maximum concentration of Ag^+ in g/l?

Exercise 8

What would be the maximum amount of AgCl that could dissolve in sea water in g/l and ppm?

This much AgCl could be soluble in sea-water, which is about half the amount actually found as listed earlier. Therefore, sea-water is not saturated in AgCl.

Table I lists the solubility product constants of a number of compounds at 25°C.

TABLE I

$Mg(OH)_2$	9.0×10^{-12}	$BaSO_4$	1.5×10^{-9}
$Ca(OH)_2$	1.3×10^{-6}	$Mn(OH)_2$	2.0×10^{-13}
$CaCO_3$	4.7×10^{-9}	$Fe(OH)_3$	6.0×10^{-38}
$CaSO_4$	2.4×10^{-5}	$Al(OH)_3$	5.0×10^{-33}
$AgCl$	3.0×10^{-10}	$Zn(OH)_2$	3.0×10^{-17}
		$Ca_3(PO_4)_2$	1.0×10^{-27}

Using these constants, the solubility of the various compounds can be calculated. However, it is important for the student to remember that he is working with solubility product constants. For example, to calculate the solubility of $Ca(OH)_2$ in water at 25°C, we proceed as follows:

$$Ca(OH)_2 \rightarrow Ca^{++} + 2(OH^-)$$

$$K_i = [Ca^{++}][OH^-]^2$$

Let X = the solubility of the $Ca(OH)_2$; then $X = [Ca^{++}]$ and $2X = [OH^-]$

$$K_i = 1.3 \times 10^{-6} = X \times (2X)^2 = 4X^3$$

$$X^3 = 0.33 \times 10^{-6}$$

$X = 0.68 \times 10^{-2}$ moles/liter x 74 grams/mole = 0.500 grams/liter is the solubility of $Ca(OH)_2$ at 25°C.

Exercise 9

What is the solubility of $Al(OH)_3$ in water at 25°C? Use Table #1.

If the ionization of a compound produces H^+ or OH^- ions, then the ionization product constant can be calculated by determining the pH of the substance in water at - say - 25°C. For example, a saturated solution of $Mg(OH)_2$ has a pH = 10.41, what is its ionization product constant?

$$pH = 10.41 = -\log [H^+]$$

$$[H^+] = 3.85 \times 10^{-11}, \quad [OH^-] = 2.60 \times 10^{-4}$$

Therefore, $Mg(OH)_2 \rightleftharpoons Mg^{++} + 2(OH^-)$

$$K_i = [Mg^{++}][OH^-]^2$$

From the equation, it can be seen that the $[Mg^{++}]$ is 1/2 that of the $[OH^-]$. Thus the $[Mg^{++}] = 1.30 \times 10^{-4}$. Substituting these values in the equation:

$$K_i = (1.30 \times 10^{-4})(2.60 \times 10^{-4})^2$$

$$K_i = 9.0 \times 10^{-12}$$

Exercise 10

What is the ionization product constant for a saturated solution of $Mn(OH)_2$ which has a pH = 10.53?

Students are often confused by the convention of doubling or halving the OH^-, while at the same time squaring the value in the ionization constant equation. However, if the mathematical and chemical equations are followed, these expressions will be clear.

Another example may help drive home the concept: calculate the solubility and pH of a saturated solution of $Fe(OH)_3$.

$$Fe(OH)_3 \longrightarrow Fe^{+++} + 3(OH^-)$$

$$K_i = [Fe^{+++}][OH^-]^3 = 6 \times 10^{-38}$$

Let $X = Fe^{+++}$, then $3X = OH^-$

$$(X) \times (3X)^3 = 6 \times 10^{-38}$$

$$27X^4 = 6 \times 10^{-38}$$

$$X^4 = 37 \times 10^{-40}$$

$$X^2 = 6.1 \times 10^{-20}$$

$$X = 2.47 \times 10^{-10} \text{ moles/liter} = [Fe^{+++}]$$

But, since $[OH^-] = 3[Fe^{+3}]$, then:

$$3X = 7.40 \times 10^{-10} \text{ moles/liter} = [OH^-]$$

$$[H^+] = 1.35 \times 10^{-5}, \text{ pH} = 4.89$$

Exercise 11

What is the solubility of a saturated solution of $Ca_3(PO_4)_2$? Note you will have to use logarithms to obtain a value for X.

You may have found Exercise 11 rather difficult due to the difficulty in taking a 1/5 root. Try one additional exercise to restore your confidence.

Exercise 12

What is the solubility and pH of a saturated solution of $Zn(OH)_2$?

Demonstration: Prepare a saturated solution of $Zn(OH)_2$ by heating about 0.1 gram of solid $Zn(OH)_2$ in 100 ml of water. Cool to room temperature (25°C) and measure the pH using the pH meter. How does this measured pH compare to that calculated in Exercise 12?

ANSWERS

A. Pretest

1. .004 M $Ca(OH)_2$ gives .008 M OH^-, so pH = 11.9
2. $K = [Mg^{++}] [OH]^2$
3. $[OH] = 1.3 \times 10^{-4}$, pH = 10.1
4. (a) 3.9×10^{-5} mole/
   (b) 9.1 ppm.
5. 2×10^{-10}
6. 2.4×10^{-7} mole Ca^{++}/liter
7. (3)
8. $K = 3 \times 10^{-17}$

B. Study Guide

1. $K_i = \frac{\text{Products}}{\text{Reactants}} = \frac{[Ag^+][Cl^-]}{[AgCl]}$

2. $K_i = [Ag^+][Cl^-]$

3. $K_i = X^2 = (1.75 \times 10^{-5})^2 = 3.0 \times 10^{-10}$

4. $16{,}200 \text{ ppm} = \frac{16{,}200 \text{ parts}}{1{,}000{,}000 \text{ parts}} = \frac{16{,}200\text{g}}{1{,}000{,}000\text{g}}$

   since 1 liter water = 1000g.

   $16{,}200 \text{ ppm} = \frac{16{,}200\text{g}}{1{,}000 \text{ liters}} = 16.2\text{g/l}.$

5. $\text{moles} = \frac{\text{weight}}{\text{molecular weight}} = \frac{16.2}{35.5} = .46 \text{ moles/liter}$

6. $K_i = [Ag^+][Cl^-] = [Ag^+][.46] = 3.0 \times 10^{-10}$

   $[Ag^+] = \frac{3.0 \times 10^{-10}}{0.46} = 6.5 \times 10^{-10} \text{ moles/liter}$

7. $6.5 \times 10^{-10} \times 108 = 7.0 \times 10^{-8}\text{g } Ag^+\text{/liter}$

8. A. $6.5 \times 10^{-10} \times 143 = 9 \times 10^{-8}\text{g AgCl/liter}$

   B. $\frac{9 \times 10^{-8}}{1000} \times \frac{1000}{1000} = \frac{9 \times 10^{-5}}{1{,}000{,}000} = 9 \times 10^{-5} \text{ ppm.}$

9. $Al(OH)_3 \rightarrow Al^{+++} + 3OH^-$

   $K_i = [Al^{+++}][OH^-]^3 = 5.0 \times 10^{-33}$

   Let X = the solubility of $Al(OH)_3$

   Then $X = [Al^{+++}]$ Each $Al(OH)_3$ that dissolves produces Al^{+++}

   $3X = [OH^-]$ Each $Al(OH)_3$ that dissolves produces three OH^-'s.

   $K_i = 5.0 \times 10^{-33} = [X][3X]^3$

   $5.0 \times 10^{-33} = 27X^4$

   $X^4 = .185 \times 10^{-33}$

   $X^4 = 1.85 \times 10^{-34}$

   $X^2 = 1.36 \times 10^{-17} = 13.6 \times 10^{-18}$

   $X = 3.7 \times 10^{-9}$

The solubility of $Al(OH)_3$ in water, at 25°C. is 3.7×10^{-9} moles/liter, which is much less than $Ca(OH)_2$.

10. pH = 10.53

$-\log[H] = 10.53$

$\log[H] = -10.53$

$\log[H] = -11 + .47$

$[H^+] = 2.95 \times 10^{-11}$

$[H^+][OH^-] = 1 \times 10^{-14}$

$(2.95 \times 10^{-11})[OH^-] = 1 \times 10^{-14}$

$[OH^-] = 3.4 \times 10^{-4}$

$K_i = [Mn^{++}][OH^-]^2$

$K_i = (X)(2X)^2$ NOTE: $[Mn^{++}] = 1/2\ [OH^-]$

$K_i = (1.7 \times 10^{-4})(3.4 \times 10^{-4})^2 = (1.7 \times 10^{-4})(11.6 \times 10^{-8})$

$K_i = 2 \times 10^{-13}$

11. $Ca_3(PO_4)_2 \rightarrow 3Ca^{++} + 2\ PO_4^{---}$

$K_i = 1.0 \times 10^{-27} = [Ca^{++}]^3\ [PO_4^{---}]^2$

Let X = solubility of $Ca_3(PO_4)_2$, then $[Ca^{++}] = 3X$ and $[PO_4^{---}] = 2X$

$1.0 \times 10^{-27} = (3X)^3(2X)^2$

$1.0 \times 10^{-27} = (27X^3)(4X^2)$

$1.0 \times 10^{-27} = 108X^5$

$X^5 = 9.3 \times 10^{-30}$

There are several ways to solve this problem, but all are basically the same. To take the nth root of any number, divide the logarithm of the number by n and then find the anti log. Thus to obtain the log of 9.3×10^{-30}, remember that an exponent is a log and that we add logs when multiplying.

$\log 9.3 \times 10^{-30} = -30 + .966 = 20.966 - 50$

Obviously, 20 - 50 = -30; -50 allows us to divide by 5 and end with 10. Therefore,

$(20.966 - 50) \div 5 = 4.193 - 10$

The anti log of .193 = 1.56 and the exponent equals (4 - 10) = -6. Thus the answer is 1.56×10^{-6}.

12. $Zn(OH)_2 \rightarrow Zn^{++} + 2OH^-$

$K_i = 3.0 \times 10^{-17} = [Zn^{++}][OH^-]^2$

Let X = solubility of $Zn(OH)_2$

Then $[Zn^{++}] = X$ and $[OH^-] = 2X$

12. (con) $3.0 \times 10^{-17} = (X)(2X)^2$

$3.0 \times 10^{-17} = 4X^3$

$X^3 = 0.75 \times 10^{-17}$

$X^3 = 7.5 \times 10^{-18}$

$X = 2.0 \times 10^{-6}$ moles/liter

$[OH^-] = 2X = 4.0 \times 10^{-6}$

$[H^+] = \frac{(1 \times 10^{-14})}{4.0 \times 10^{-6}} = 0.25 \times 10^{-8} = 2.5 \times 10^{-9}$

pH = $-\log 2.5 \times 10^{-9} = -(-9 + 0.40) = 8.6$

pH = 8.60

pH AND HYDROGEN ION CONCENTRATION

SUMMARY

This mini-course develops the concepts of hydrogen ion concentration and pH. Logarithms are reviewed. The operation of a pH meter and the glass electrode is introduced.

The measurement of pH, acidity, and alkalinity is of importance to all chemists, but is of particular importance to the water chemist. But measurements alone are not enough, the chemist must understand the underlying principles and be able to convert pH to hydrogen ion concentration and vice versa.

PREREQUISITES

Before studying this mini-course, you should be able to:

a) Use exponents in multiplications and divisions.

b) Use a logarithmic table.

c) State the difference between strong and weak acids and strong and weak bases.

d) Perform percentage calculations.

ACKNOWLEDGEMENT

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OBJECTIVES

At the completion of this mini-course, you should be able to:

1. Define logarithms and the use of logarithms in pH calculations.

2. Define pH.

3. When given values of $[H^+]$, $[OH^-]$, or pH, calculate the other two values.

4. Given the total concentration of a weak acid or a weak base, and the pH, calculate the percent ionization of that substance.

5. Describe the operation of a pH meter, including the operation of the glass electrode, and use the pH meter to determine pH of a given solution.

6. Define "buffer solution".

PRETEST

Choose the correct answer. Only one answer is correct.

1. $10^5 \times 10^3 =$ __________.
   a) 10^{15} b) 10^2 c) 18 d) 1,000,000 e) 100,000,000
2. $\frac{10^{-5} \times 10^8}{10^{-7}} =$ ______________.
   a) 10^6 b) 10^{20} c) 10^{10} d) 10^{33} e) 10^{-4}
3. If $10.^{0.6021} = 4$, the logarithm of 4 to the base 10 is: ______________.
   a) 10^4 b) 4 c) 4^{10} d) 6.021 e) 0.6021
4. The logarithm of 900 (to the base 10) is 2.9542. This can be written in an exponentical form as: ______________.
   a) $\log 10^{900} = 2.9542$
   b) $10^{.9542} = 900$
   c) $10^{.29542} = 900$
   d) $10^{2.9542} = 900$
   e) $10^{900} = 2.9542$
5. "pH" is defined as: ______________.
   a) $pH = H^+$
   b) $pH = \log H^+$
   c) $pH = -\log H^+$
   d) $pH = - H^+$
   e) $pH = \log p + \log H^+$
6. If a solution has a pH of 4.5, the molar concentration of H^+ per liter is: ______________.
   a) $10^{4.5}$ b) 4.5^{10} c) $10^{-5.5}$ d) $10^{5.5}$ e) $10^{-4.5}$
7. The pH of black coffee is: ______________.
   a) neutral
   b) weakly acidic
   c) strongly acidic
   d) weakly basic
   e) strongly basic
8. The pH of a solution is 3.45. The H^+ of this solution is: ______________.
   a) $10^{3.45}$ b) $10^{-3.45}$ c) 3.548×10^{-4} d) 3.548×10^4 e) 3.548
9. A solution of 0.01 N sodium hydroxide has a pH of: ______________.
   a) $10^{.01}$ b) $-\log .01$ c) $\log .01$ d) 10^{-12} e) 12
10. A 0.01 N of ammonium hydroxide has a pH of 10.6. The percentage ionization is approximately equal to: ______________.
    a) 2.512×10^{-11} b) 4×10^{-3} c) 4×10^{-4} d) 4 e) 3.4

pH and Hydrogen Ion Concentration

A review of coefficients and logarithms is necessary in order to understand pH and $[H^+]$. We know:

$10^0 = 1$	$10^{-1} = 0.1 = 1/10$
$10^1 = 10$	$10^{-2} = 0.01 = 1/100$
$10^2 = 100$	$10^{-3} = 0.001 = 1/1000$
$10^3 = 1000$	$10^{-6} = 0.000001 = 1/1,000,000$
$10^6 = 1,000,000$	

Exercise 1

Do the following conversions:

a. $10^5 =$

b. $0.0001 =$

c. $100,000,000,000 =$

We also know that in multiplication and division of exponents:

$$10 \times 100 = 1,000 = 10^1 \times 10^2 = 10^3$$

$$100 \times 10,000 = 1,000,000 = 10^2 \times 10^4 = 10^6$$

$$\frac{100,000}{100} = 1,000 = \frac{10^5}{10^2} = 10^{5-2} = 10^3$$

$$\frac{100}{1,000,000} = 0.0001 = \frac{10^2}{10^6} = 10^{2-6} = 10^{-4}$$

Exercise 2

Do the following computations:

a. $10^5 \times 10^2 =$

b. $\frac{10^5}{10^2} =$

c. $\frac{10^5 \times 10^3}{10^2} =$

d. $\frac{10^{-6} \times 10^8}{10^{-4}}$

In other words, we add exponents when multiplying and subtract exponents when dividing. This is straightforward when even powers are involved, but what about: $10^x = 5$. In this case, 10 raised to what power equals 5; or, what is "x" in the above expression?

Is it not obvious from the following

$$10^0 = 1$$
$$10^x = 5$$
$$10^1 = 10$$

that "x" must lie between 0 and 1. The value of "x" is found in a table of logarithms to the base 10 to be 0.6999. So,

$$10^{.699} = 5 \quad \text{or} \quad \log_{10}5 = 0.699$$

It also follows that the logarithms of 50, 500, 5,000,000 are:

$$50 = (5 \times 10) = 10^{.699 + 1} = 10^{1.699}$$

$$\text{therefore, } \log_{10}50 = 1.699$$

$$500 = (5 \times 100) = 10^{.699 + 2} = 10^{2.699}$$

$$\text{therefore, } \log_{10}500 = 2.699$$

$$5{,}000{,}000 = (5 \times 1{,}000{,}000) = 10^{.699 + 6} = 10^{6.699}$$

$$\text{therefore } \log_{10}5{,}000{,}000 = 6.699$$

Thus, an exponent is a logarithm.

Exercise 3

Using a logarithm table, calculate:

a. log 3 =

b. log 75 =

c. log 0.01 =

d. log 0.008 =

Turning now to hydrogen ions and hydroxyl ions in water, it was previously said that:

$$[H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14} = K_w$$

In general, then:

$$10^y = N$$

Taking logs of both sides of this equation:

$$y \log 10 = \log N$$

$$\log N = y \times 1 \text{ (the log 10=1)}$$

$$y = \log N$$

Since the $[H^+] = [OH^-]$, pure water is neutral - it is neither acidic or basic.

Exercise 4

Using the K_w expression, calculate the following:

a. If $[H^+] = 1 \times 10^{-6}$, calculate $[OH^-]$

b. If $[H^+] = 1 \times 10^{-2}$, calculate $[OH^-]$

c. If $[OH^-] = 1 \times 10^{-5}$, calculate $[H^+]$

d. If $[H^+] = 1 \times 10^{-12}$, calculate $[OH^-]$

If, however, the $[H^+] = [10^{-6}]$, then the $[OH^-] = 10^{-8}$, and the solution is slightly acid. Quantitatively, the $[H^+]$ has been increased ten fold. In like manner, a solution whose $[H^+] = 10^{-4}$ has $10^3 = 1{,}000$ times more H^+ than water.

Exercise 5

Which of the above would you label as "neutral"? as "slightly acidic"? as "strongly acidic"? or as "basic"?

The definition of pH

Suppose, in the following, your finger covers everything but the exponent - it covers the 10 and the (-). All that is left is 7, 6, 4, 2, 1. By definition, the pH of the above solutions are:

$[H^+]$	pH	Nature of solution
10^{-7}	7	Pure water
10^{-6}	6	Very weak acid
10^{-4}	4	Weak acid
10^{-2}	2	Strong acid
10^{-1}	1	Very strong acid

Since the exponent without the (-) is the pH, and the exponent *is* a logarithm, then:

$$pH = -\log [H^+]$$

Going in the opposite direction:

$[H^+]$	pH	Nature of solution
10^{-8}	8	Very weak base
10^{-10}	10	Weak base
10^{-12}	12	Strong base
10^{-13}	13	Very strong base

Exercise 6

Calculate the pH of each of the following:

a. 1×10^{-5} M H^+
1×10^{-11} M H^+
1×10^{-4} M OH^-

Calculate the H^+ concentration and the OH^- concentration for the given pH values:

b. 2
8
13

As long as the pH equals a whole number, it is easy to switch to $[H^+]$ or from $[H^+]$ to pH. Now to calculate the $[H^+]$ if the pH = 5.33.

$$pH = -\log [H^+]$$

$$5.33 = -\log [H^+] \text{ or } \log [H^+] = -5.33$$

The right side of an algebraic equation must equal the left side, so -5.33 must be a logarithm. (It is also the definition of pH). To handle a negative log, the above is changed to:

$$\log [H^+] = -5.33 = -6.00 + 0.67$$

The number whose log = 0.67 is 8.26; the number whose log = -6.00 is 10^{-6}

Thus, $[H^+] = 8.26 \times 10^{-6}$, since in multiplication we add logarithms.

Suppose the $[H^+] = 6.26 \times 10^{-13}$, what is the pH?

$$pH = -\log [6.26 \times 10^{-13}] \quad \text{(the log of 6.26 = 0.797)}$$

$$pH = -(0.797 - 13) = 12.20$$

Exercise 7

a. Use a table of logarithms or a slide rule to compute the pH of the following:

$[H^+] = 2.0 \times 10^{-5}$
$[H^+] = 4.5 \times 10^{-8}$
$[OH^-] = 6 \times 10^{-2}$

b. Calculate the $[H^+]$ for:

pH = 5.51
pH = 8.75
pH = 1.33

Strong acids and bases

The groundwork is now laid to express quantitatively what is meant by a strong acid and a strong base. For example, a 0.1 N of H_2SO_4 means that:

The $[H^+]$ = 0.1 mole/liter, and thus the pH = 1.0, assuming complete ionization.

The $[H^+]$ of a 0.01 N H_2SO_4 solution = 0.01 moles/liter, and therefore the pH = 2.0

A strong acid or a strong base is one which ionizes essentially 100% in water. Examples are H_2SO_4, HCl, HNO_3 and $HClO_4$ for acids, and any soluble metal hydroxide, such as NaOH or KOH.

For a 0.1 N solution of NaOH, the $[OH^-]$ = 0.1 moles/liter, thus:

$$K_w = 10^{-14} = [H^+] \times [OH^-] = [H^+][10^{-1}]$$

$$[H^+] = 10^{-13}, \ pH = 13.0$$

Weak acids and bases

A weak acid or base will not ionize completely in water. Often acids, like acetic acid, and bases, such as NH_4OH, ionize less than 1%.

Referring to the previous mini-course, 4.0165g. of potassium acid phthalate was dissolved in distilled water in order to standardize a 0.5 N solution of NaOH. The initial pH = 4.00. We now know that this means that the

$$[H^+] = 10^{-4} = 0.0001 \text{ moles/liter of } H^+$$

Actually there was present:

$$\frac{4.0165}{204.22} = 0.0197 \text{ moles/liter of potassium acid phthalate}$$

Thus $\frac{0.0001}{0.0197} = 0.005 = 0.5\%$ of the potassium acid phthalate is present as H^+. Conversely, 99.5% is not ionized.

Thus very few H^+ were initially present, but as these were neutralized by the NaOH solution, more and more of un-ionized potassium acid phthalate became ionized to react with the additional NaOH, until at pH = 7.0, all of the potassium acid phthalate had ionized and reacted with the NaOH solution.

Exercise 8

a. A 0.1 mole/liter solution of weak acid, HX, was found to have a pH 4.20. Calculate the percentage of ionization:

b. A 0.05 M solution of the weak base NH_4OH gave a pH of 10.9. What is the percentage ionization of this solution?

The pH meter and glass electrodes

Few instruments are more rugged, dependable and as simple to use as a pH meter. Basically it is a potentiometer - a device for measuring small electrical potentials, or voltages. It is a milli-volt meter. Actually, pH is an abbreviation of "potential of the H^+ concentration".

As in all electrochemical measurements, an electrial potential involves two electrodes. One of these in this case - is called the reference electrode, and the other the indicating electrode. This consists of metallic mercury, mercurous chloride and a solution of potassium chloride. The indicating electrode consists of a bulb made of a special thin glass which is sensitive to H^+. The glass electrode is the first of the so-called specific ion electrodes. Historically it was introduced about 40 years ago and has been constantly improved since then. The bulb of the glass electrode is filled with a solution of fixed hydrogen ion content: though impermeable to aqueous solutions, the bulb acts as a glass membrane which establishes a potential - or electrical pressure - which is proportional to the difference in hydrogen ion concentration between the liquid inside and outside the glass bulb. The pH meter amplifies this potential and displays it by a needle sweeping a scale marked from 0 to 14. The neutral point of 7 is usually in the middle of the scale.

Before using a pH meter, it should be calibrated against a buffer solution whose pH is near that of the pH to be measured. More will be said about buffers later on, but for the present let us think of a buffer as an aqueous solution that tends to maintain a constant pH even though small amounts of acids and bases may be present inadvertantly.

Exercise 9

Measure the pH of the following solutions, then label each as

(a) strong acids
(b) weak acids
(c) neutral
(d) weak bases
(e) strong bases

H_3PO_4, HNO_3, KCl, Na_2CO_3, CH_3COOH, NH_4OH

ANSWERS

PRETEST

1) c
2) c
3) e
4) d
5) c
6) e
7) b
8) c
9) e
10) d

STUDY GUIDE

1. A. $10^5 = 100{,}000$
   B. $0.0001 = 1 \times 10^{-4}$
   C. $100{,}000{,}000{,}000 = 1 \times 10^{11}$

2. A. $10^5 \times 10^2 = 10^7$
   B. $\frac{10^5}{10^2} = 10^3$
   C. $\frac{10^5 \times 10^3}{10^2} = 10^6$
   D. $\frac{10^{-6} \times 10^8}{10^{-4}} = 10^6$

3. A. $\log 3 = .477$
   B. $\log 75 = 1.875$
   C. $\log 0.01 = \log 1 \times 10^{-2} = -2 \quad [0 + (-2) = -2]$
   D. $\log 0.008 = \log 8 \times 10^{-3} = -3 + .903 = -2.097$

4. A. $[H^+] = 1 \times 10^{-6}; \; K_w = [H^+][OH^-] = 1 \times 10^{-14}$
   $[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-6}} = 10^{-8}$
   B. $[OH^-] = \frac{1 \times 10^{-14}}{10^{-2}} = 10^{-12}$
   C. $[H^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-5}} = 10^{-9}$
   D. $[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 1 \times 10^{-2}$

5. A. Slightly acidic
   B. Strongly acidic
   C. Basic
   D. Strongly basic

6. A. pH = 5

pH = 11

pH = 10

B. $[H^+] = 10^{-2}$, $[OH^-] = 10^{-12}$

$[H^+] = 10^{-8}$, $[OH^-] = 10^{-6}$

$[H^+] = 10^{-13}$, $[OH^-] = 10^{-1}$

7. A. $[H^+] = 2.0 \times 10^{-5}$

$pH = -\log [H^+] = -\log 2.0 \times 10^{-5}$

$pH = -[.30 + (-5)] = -(-4.70) = 4.70$

$pH = -\log 4.5 \times 10^{-8}$

$pH = -[.65 + (-8)] = 7.35$

$[OH^-] = 6 \times 10^{-2}$; $[H^+] = \frac{10^{-14}}{6 \times 10^{-2}} = 1.66 \times 10^{-13}$

$pH = -[.22 + (-13)] = 12.78$

B. $pH = -\log [H^+]$

$\log [H^+] = -5.51 = -6.0 + .49$

$[H^+] = 3.1 \times 10^{-6}$

$\log [H^+] = -8.75 = -9.0 + .25$

$[H^+] = 1.8 \times 10^{-9}$

$\log [H^+] = -1.33 = -2.00 + .67$

$[H^+] = 4.7 \times 10^{-2}$

8. A. pH = 4.20

$\log [H^+] = -4.20 = -5 + .8$

$[H^+] = 6.3 \times 10^{-5}$

$HX \longrightarrow H^+ + X^-$, $[HX] \approx 0.1$

$[H^+] = 6.3 \times 10^{-5}$

$\text{Ionization} = \frac{6.3 \times 10^{-5}}{0.1} \times 100 = 6.3 \times 10^{-2} = .063\%$

B. pH = 10.9

$\log [H^+] = -10.9 = -11 + .1$

$[H^+] = 1.3 \times 10^{-11}$

$[OH^-] = 7.7 \times 10^{-4}$

$NH_4OH \longrightarrow NH_4^+ + OH^-$, $[NH_4OH] \approx .05$

$[OH^-] = 7.7 \times 10^{-4}$

$\text{Ionization} = \frac{7.7 \times 10^{-4}}{0.05} \times 100 = 1.54\%$

9.	H_3PO_4	strong acid
	HNO_3	strong acid
	KCl	neutral
	Na_2CO_3	weak base
	CH_3COOH	weak acid
	NH_4OH	weak base

ACIDS AND BASES

SUMMARY

This mini-course deals with the definitions of acids and bases, the concept of strong and weak acids and bases and the methods of standardizing aqueous solutions of acids and bases.

ACKNOWLEDGEMENT

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PREREQUISITES

Before studying this mini-course, the student should be able to:

1. Define "mole" and apply the concept of mole in chemical equations.
2. Calculate the molecular weight of a compound using the periodic table.
3. State the operational definitions of acids and bases.
4. Define H^+, OH^-, and pH.
5. Handle a pipette and a burette and perform acid-base titrations using indicators.

OBJECTIVES

At the conclusion of this mini-course, the student should be able to:

1. State the concepts of acids and bases as applied to aqueous solutions.
2. Calculate the molarity and normality of the solution, given the weight and formula of an acid or base dissolved in a stipulated volume of water.
3. Calculate the volume required to make an aqueous solution of known strength, given the purity and density of a solution.
4. State the gravimetric and/or volumetric procedure for standardizarions of acids and bases.
5. Calculate the normality of an acid or base, given the appropriate volumetric or gravimetric data.
6. Use a pH meter or titrating an acid or base, and plot the data.
7. Define strong and weak acids and strong and weak bases and recognize at least one example of each.

PRETEST

Choose the correct answer for the following questions. Only one answer is correct.

1. If the hydrogen ion concentration of a solution is 10^{-4} moles per liter, the pH of the solution is:

a) 10^{-4}, b) -4, c) 4, d) 40, e) -40.

2. The pH of a solution is 10. The hydrogen ion concentration in moles per liter is:

a) 10, b) 10^{-10}, c) 10^{-4}, d) 4, e) 10^{4}

3. The pH of a solution is 3. The hydroxyl ion concentration in moles per liter in this solution is:

a) 11, b) 10^{-3}, c) 10^{-7}, d) 10^{-11}, e) 10^{3}

4. A 1 N solution of acetic acid (CH_3COOH) contains the following weight of it in one liter of its solution:

a) $\frac{60}{1}$, b) $\frac{60}{2}$, c) $\frac{60}{3}$, d) $\frac{60}{4}$, e) $\frac{60}{8}$

5. The strength of a 1 N solution of phosphoric acid, H_3PO_4 is equivalent to:

a) 1 N, b) 4 N, c) N, d) 2 N, e) 7 N

6. The label of the container of a standard solution of sulfuric acid has been eaten away! In order to determine its strength, this solution was titrated against a 0.125 N solution of sodium hydroxide. 20 ml. of the sodium hydroxide solution was neutralized by 25 ml. of the acid. The normality of the acid is:

a) 0.16 N, b) 0.4 N, c) 4 N, d) 1 N, e) 0.1 N

7. 20 ml. of a solution of hydrochloric acid on treatment with an excess solution of silver nitrate yielded 0.4298 g. of silver chloride. The normality of the hydrochloric acid is:

a) 1 N, b) 0.1095 N, c) 0.4298 N, d) 1.5 N, e) 0.15 N

8. 20 ml. of a solution of potassium hydroxide requires 0.6126 g. of potassium hydrogen phthalate (KHP) for neutralization . The weight of KHP is 204.2. The strength of the potassium hydroxide solution is:

a) 6.126 N, b) 0.6126 N, c) 3.0630 N, d) 0.15 N, e) 0.30 N

9. The reason potassium acid phthalate (KHP) is often used to standardize basic solutions is:

a) it is cheap

b) it is solid, commercially available in a pure form

c) it is easily soluble in water

d) it rapidly reacts with bases

e) it is recommended by National Bureau of Standards

f) all of these are valid reasons

10. The following is a pair of weak acid and a weak base:

a) HCl; NaOH,

b) HCl; NH_4OH,

c) CH_3COOH; H_2SO_4,

d) CH_3COOH; NH_4OH,

e) KHP; KOH

ACIDS AND BASES

Hopefully, by now, student and seasoned scientist are duly impressed by the disarmingly over-simplified statement that water is H_2O and that the purest of water ionizes ever so slightly:

$$H_2O \rightarrow H^+ + OH^-$$

The student should recall that it was previously stated that, for water, the hydrogen ion concentration $[H^+] = 10^{-7}$ moles per liter and the hydroxyl ion concentration $[OH^-]$ also equals 10^{-7} moles per liter. Thus pure water contains:

$$[H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

The constant 10^{-14} is such an important number that it is designated as K_w - which is the ionization product constant for water. This never changes; this is the nature of water. No matter what we do to water, it will always be true that:

$$K_w = [H^+][OH^-] = 10^{-14} \text{ for pure water.}$$

Suppose, somehow, the concentration of H^+ in a sample of water is increased so that $[H^+] = 10^{-6}$ (Remember that 10^{-6} is larger than 10^{-7}). The concentration of OH^- must be reduced to satisfy the above requirement. Thus if $[H^+] = 10^{-6}$, the $[OH^-]$ must equal 10^{-8} so that:

$$K_w = [H^+][OH^-] = 10^{-6} \times 10^{-8} = 10^{-14}$$

If the hydrogen ion concentration is increased further, the relationship must always be the same.

Exercise 1 - Complete the following table. Calculate missing values.

$[H^+]$	$[OH^-]$	K_w	pH
10^5			
	10^{-10}		
10^{-3}			
	10^{-12}		
10^{-1}			
			6.0

Acids

An acid is a substance which, so far as water chemistry is concerned, produces H^+ in aqueous solutions. When hydrochloric acid - HCl - is dissolved in water it produces H^+ and Cl^-:

$$HCl \xrightarrow{H_2O} H^+ + Cl^-$$

Thus HCl is an acid, and a strong acid, since it dissociates into H^+ ions and Cl^- ions. A 0.1 N solution of HCl would have a $[H^+] = 10^{-1}$.

Acetic acid is a relatively weak acid since it does not form a large concentration of H^+ when dissolved in water. These differences will be dealt with quantitatively when ionization constants are discussed.

For the present, our concern is an understanding of how and why chemists use acids and bases - quantitatively - in the laboratory. First, the "how".

If a mole (abbreviation for molecular weight) of HCl is dissolved in a liter of water, this means that:

$$\frac{HCl}{36.5g} \xrightarrow{H_2O} \frac{H^+}{1g} + \frac{Cl^-}{35.5g}$$

Quite simply, the chemist says that if one mole of HCl (36.5g.) is present in one liter of an aqueous solution, it is a molar solution of HCl. It will be seen from the above equation that the solution contains one mole of H^+ per liter of solution.

If a mole of H_2SO_4 is dissolved in a liter of water, then:

$$\frac{H_2SO_4}{98g} \xrightarrow{H_2O} \frac{2H^+}{2g} + \frac{SO_4^=}{96g}$$

Again, 98g. of H_2SO_4 dissolved in enough water to make liter solution is a molar solution of H_2SO_4. Obviously, however, there is a big difference, since the molar solution of H_2SO_4 contains two moles of H^+ per liter of the solution: twice as much as the molar solution of HCl.

Exercise 2

Calculate the number of moles per liter of the following acids and H^+.

Hydrochloric Acid			Sulfuric Acid		
g/l	moles	H^+/l	g/l	moles	H^+/l
73.0			49.0		
3.65			.49		
.0365			98		
.183			.0245		

Frequently, if not most of the time, the chemist's main interest in an acid solution is the hydrogen ion concentration, so a term is used which puts these - and all other acids - on an equal footing. The name of the game is to have one mole of H^+ present in one liter of the solution - this is called a "normal" solution.

Since a molar solution of HCl contains one mole of H^+ per liter of the solution, a molar solution of HCl is the same as a normal solution of HCl.

It should be obvious that to make a normal solution of H_2SO_4, 49g. of H_2SO_4 are dissolved in one liter of water, thus obtaining one mole of H^+ per liter. That is, 49g. is 1/2 the molecular weight of H_2SO_4.

The same reasoning is applied to the other acids commonly used in the laboratory:

	Needed per liter to make	
	Molar solution	Normal solution
$HNO_3 \rightarrow H^+ + NO_3^-$	63g.	63g.
$CH_3COOH \rightarrow H^+ + CH_3COO^-$	60	60
$H_3PO_4 \rightarrow 3H^+ + PO_4^{---}$	98	33

In like manner, other strength solutions are made proportionally:

	HCl	H_2SO_4
0.1 N	3.65g/1	4.9g/1
0.5	18.3	24.5
2.0	73.	98.

Exercise 3

Calculate the normality of each of the solutions in Exercise 2.

Actually, it is easier and more convenient to measure corrosive liquids in a volumetric cylinder than to weigh them on a balance. Thus to measure out the required amount of HCl, H_2SO_4, and other acids note that the labels on the bottles of these concentrated acids state:

	Mol. wt.	Assay	Density
HNO_3	73	70-71%	1.42 g/ml
H_2SO_4	98	95-98	1.84
H_3PO_4	98	85	1.73
HCl	36.5	36-38	1.19
CH_3COOH	60	98	1.07

The volume equivalent to 36.5g. of HCl is calculated as follows:

$$d = \frac{m}{V} \quad : V = \frac{m}{d}$$

$$V = \frac{36.5}{1.19} = 30.6 \text{ ml of } 100\% \text{ HCl}$$

$$V = \frac{30.6}{.37} = 83 \text{ ml of } 37\% \text{ HCl}$$

Similar calculations show that 27 ml of concentrated H_2SO_4 are required to make one liter of a 1 N. solution of H_2SO_4. Obviously, 1/10 of these amounts would be used to make 0.1 N. solutions, and so on.

Exercise 4

Calculate the volumes of each of the following concentrated acids needed to prepare one liter of the following:

1 N HNO_3
.1 N H_3PO_3
.5 N CH_3COOH

Bases

The same procedure is followed for making molar and normal solutions of bases. Three bases are commonly used in the laboratory:

$$NaOH \xrightarrow{H_2O} Na^+ + OH^-$$
$$KOH \xrightarrow{H_2O} K^+ + OH^-$$
$$NH_4OH \xrightarrow{H_2O} NH_4^+ + OH^-$$

All of these yield one mole of OH^- per mole of base so that in all cases a molar solution is the same as a normal solution. In two respects the above bases differ. NaOH and KOH are strong bases and they are solids so that the amount wanted is weighed out on a balance:

40g/1 of NaOH for a 1 N. solution

56g/1 of KOH for a 1 N. solution

NH_4OH is a weak base and solutions are made by measuring out a certain volume from a bottle of concentrated NH_4OH, using the data given on the label of the bottle - exactly as in making up solutions of acids.

Exercise 5

Obtain the necessary data from a stock bottle of NH_4OH, and calculate the volumes of concentrated base required to prepare:

(a) 1.0 1 of a 1 molar solution

(b) 1.0 1 of a 1 normal solution

(c) 5.0 1 of a 0.5 normal solution

Accuracy is an attribute expected of every chemist, and it should be obvious that it isn't possible to measure the above acids and bases with any degree of exactness. Therefore, after the solutions of acids and bases have been made, their strength must be accurately determined. This is done either gravimetrically (by weighing something on a chemical balance) or volumetrically (by measuring a volume using a good burette).

Exercise 6

Why are the solutions of standard acids and bases prepared by diluting the stock solution of insufficient accuracy?

Neutralization

Throughout the above the term "neutralization" has been used repeatedly without explanation of definition. But it has been emphasized - perhaps too often - that acids are substances which produce H^+ in aqueous solutions and alkalies are substances which produce OH^- in aqueous solutions. Furthermore, it was said that the H^+ and OH^- in water are joined together so tightly that it takes a mighty force to separate them. Conversely, then, there is a great tendency for these ions to join together to form water - if they can. This is exactly what happens when an acid is added to a base: the H^+ of the acid combine with the OH^- of the base to form water:

$$H^+Cl^- + Na^+OH^- \longrightarrow Na^+Cl^- + H_2O$$

Since there are the same amount of Na^+ and Cl^- on both sides of the equation, it may be written simply as:

$$H^+ + OH^- \longrightarrow H_2O$$

If an acid solution is added to an alkaline solution so that the $[H^+]$ of the acid exactly equals the $[OH^-]$ of the alkali, then water is formed - plus a salt - and we say that the solution is neutral. The process of exactly balancing an acid with a base is therefore called neutralization.

Gravimetric standardization

H_2SO_4 lends itself to this procedure since:

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2HCl$$

$BaSO_4$ is practically insoluble as the downward arrow indicates so that it can be filtered, dried and accurately weighed on a chemical balance to four decimal places. The general procedure is to carefully measure out a volume of the solution to be standardized - say 50.0 ml - from a good burette into a 400 ml beaker containing about 200 ml of distilled water. To this is added - with constant stirring - an excess of $BaCl_2$ dissolved in about 100 ml of distilled water. A precipitate forms, but the particle size of it is so small that some of the precipitate would pass thru the pores of a filter. Therefore, the beaker is covered with a watch glass and placed in a warm place such as on the top of an oven. The small particles dissolve and reprecipitate on larger particles so that by the next morning, all the precipitate is held on a tared filter pad and Gooch crucible. After thorough washing and drying, the net weight of the precipitate is determined. Suppose, for example, a 0.5 N solution of H_2SO_4 is to be standardized and 50 ml of the solution are measured out as noted above:

$$\frac{H_2SO_4}{98} + \frac{BaCl_2}{208} \longrightarrow \frac{BaSO_4\downarrow}{233.34} + \frac{2HCl}{}$$

50 ml = 1/20 liter, so that 208/20 = 10.4g. of $BaCl_2$ would be needed to complete the precipitation of a 1 molar solution of H_2SO_4. A 1.0 N solution would require half of this, and a 0.5 N solution, half again:

$\frac{10.4}{2\times2}$ = 2.6g. $BaCl_2$ required and therefore 3.0g would assure an excess.

Suppose, using the above example, the precipitate of $BaSO_4$ weighed 3.0216g. What is the exact normality of the H_2SO_4 solution? One liter of a 1.0 N solution of H_2SO_4 should precipitate $\frac{233.34}{2}$ = 116.67g. $BaSO_4$.

Actually, it was found 50 ml precipitated 3.0216g.; therefore, 1 liter would precipitate 3.0216 x $\frac{1000}{50}$ = 60.432g. $BaSO_4$.

$$\text{Normality of the } H_2SO_4 \text{ solution} = \frac{60.432}{116.67} = 0.516 \text{ N}$$

The following reaction and the above procedure could be used for the gravimetric standardization of a solution of HCl:

$$HCl + AgNO_3 \longrightarrow AgCl \downarrow + HNO_3$$

Exercise 7

Complete and balance the following reactions:

(a) $Ca(OH)_2 + HCl \longrightarrow$

(b) $Ca(OH)_3 + H_3PO_4 \longrightarrow$

(c) $HNO_3 + NaOH \longrightarrow$

(d) $H_2SO_4 + KOH \longrightarrow$

Exercise 8

The above examples of gravimetric standardization of an acid are not acid-base reactions. Why can an acid be standardized without using neutralization?

Volumetric standardization

Since all sodium, potassium and ammonium compounds are soluble in water, their solutions cannot be standardized gravimetrically by weighing an insoluble precipitate. But an equally accurate - and easier - procedure is available.

This is known as "titration", which involves the accurate determination of the volumes of an acid and a base that just neutralize each other. The use of a pH meter (and appropriate electrodes) is usually the preferred way of doing this, otherwise an indicator (phenolphthalein, methyl orange or litmus) is used to reveal the end point. These indicators are organic materials, which possess one color in an acid medium and a different color in a basic medium:

INDICATOR	COLOR	
	ACID	BASE
PHENOLPHTHALEIN	COLORESS	RED
METHYL ORANGE	RED	YELLOW
LITMUS	RED	BLUE

Suppose it is required to determine the strength of a hydrochloric acid solution and that a standard base strength, 0.120 N is provided. 20.0 ml. of the acid is exactly measured from a burette into a beaker. A drop or two of the indicator, phenolphthalein is added to the acid in the beaker, which is placed under a burette containing the base. The initial reading is noted and the base allowed to run into the beaker with constant stirring. The addition can be rapid at first, but slowed down later and finally continued dropwise. At one point, the colorless solution in the beaker just turns red. Let 21.5 ml. be the volume of the base added to this point, called the "end point". Then the strength of the acid can be calculated by using the general relationship, which states that "equal volumes of solutions of equal strength react completely with one another":

$$V_{acid} \times N_{acid} = V_{Base} \times N_{Base}$$

where V refers to the volume and N represents the normality of the solutions. Then, 21.5 ml. X N_{acid} = 20.0 ml. X 0.120N

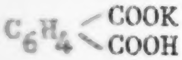
$$N_{acid} = \frac{20.0 \text{ ml.} \times 0.120N}{21.5 \text{ ml.}}$$

$$= 0.112 \text{ N}$$

Exercise 9

What is the normality of a solution of H_2SO_4 if it takes 40.0 ml of 0.513 N KOH to neutralize 45.6 ml of the H_2SO_4 solution?

Potassium acid phthalate is a pure solid acid that: can be weighed accurately on a chemical balance; is readily available and commonly used for standardizing basic solutions; has one H^+ per mole available for reacting with a base. Its formula is:



$$C_6H_4 \begin{array}{l} \diagup COOK \\ \diagdown COOH \end{array}$$

or $C_8H_5O_4K$, or KHP m.w. = 204.22

In an actual experiment, 4.0120g. of potassium acid phthalate were weighed in a 400 ml beaker. Using the above procedure, it required 40.1 ml of a NaOH solution for neutralization using phenolphthalein as the indicator. (It is good practice to use an amount of potassium acid phthalate that requires between 40 and 50 ml of the solution being standardized. This gives a good reading and avoids refilling the burette.)

$$\frac{4.0120}{40.1} \times 1000 = 100.05\text{g.}$$ of potassium acid phthalate required to neutralize 1 liter of the NaOH solution.

$$\text{Normality of the NaOH solution} = \frac{100.05}{204.22} = 0.490 \text{ N}$$

Exercise 10

45.2 ml of a KOH solution were required to neutralize 7.5578g of potassium acid phthalate. What is the normality of the KOH solution?

Separate standardizations of solutions of acids and bases gives independent values that - if they agree - leaves no doubt as to the accuracy of both determinations. By this is meant: suppose a solution of NaOH was found to be 0.490 N and a solution of H_2SO_4 was 0.518 N. Since the H_2SO_4 is stronger, one could measure out 50 ml of the NaOH. The amount of H_2SO_4 required to neutralize this should be:

$$50 \times \frac{.490}{.518} = 47.3 \text{ ml of } H_2SO_4$$

If this is the case, the chemist knows that he is ready for business. If not, checks have to be made until the figures do agree.

Due to the relative difficulty of gravimetric standardization, acid solutions are sometimes compared to the base and this value used. If a solution of KOH was found to be 0.114 N and it took 48.6 ml of HCl to neutralize 50.0 ml of the base then:

$$\begin{array}{l}\text{Normality of}\\ \text{HCl solution}\end{array} = 0.114 \times \frac{50.0}{48.6} = 0.118 \text{ N}$$

Exercise 11

The above NaOH was found to be 0.490 N. If 32.2 ml of a HCl solution were required to neutralize 25.0 ml of this NaOH solution, what is the concentration of the HCl solution?

Use of the pH meter for standardizing solutions

The previous mini-course developed the concept of pH. Instead of using an indicator to show an end point is reached, the pH meter registers neutrality with extreme accuracy.

Laboratory data for the standardization of a 0.5 N solution of NaOH using a pH meter is given below together with a plot of mls against pH. For this, 4.0165g. of potassium acid phthalate was weighed into a 400 ml beaker, enough water added to make 200 ml of solution, and the NaOH solution carefully added from a 50 ml burette.

pH	ml	pH	ml	pH	ml	pH	ml
4.00	0	5.30	26	6.20	37.5	7.00	39.5
4.33	5	5.40	28	6.31	38.0	7.30	39.7
4.61	10	5.50	30	6.48	38.5	9.00	40.0
4.88	16	5.62	32	6.51	38.7	10.95	41.0
5.05	20	5.78	34	6.61	38.9	11.30	42.0
5.12	22	5.87	35	6.70	39.1	11.73	45.0
5.20	24	5.98	36	6.81	39.3	12.02	50.0
		6.12	37	6.90	39.4		

Exercise 12

(a) Before looking at Figure 1, make up a 0.35 N solution of NaOH and, using a pH meter, obtain data similar to above by weighing out the proper amount of potassium acid phthalate.

(b) Plot the data.

(c) Calculate the normality of the KOH solution.

(d) Compare your curve with Figure 1.

The above data is plotted on Figure 1. It should be noted that smaller and smaller increments were used as the neutral point was approached.

The normality of the NaOH solution is:

$\frac{4.0165}{39.5} \times 1000 = 101.70$g. of potassium acid phthalate that would be required to neutralize 1 liter of the NaOH.

$\frac{101.70}{204.22} = 0.498$ normality of the NaOH solution.

The normality of the approximately 0.5 H_2SO_4 was determined by titrating 40.0 ml of it against the standardized NaOH:

pH	ml	pH	ml	pH	ml
1.22	0	2.15	30	3.40	35.2
1.30	5	2.23	31	3.75	35.4
1.39	10	2.35	32	6.40	35.6
1.50	15	2.41	32.5	9.15	35.7
1.60	20	2.50	33.0	9.58	35.8
1.70	22	2.60	33.5	10.31	36.0
1.80	24	2.70	34.0	10.90	36.6
1.90	26	2.90	34.5	11.50	39.0
2.00	28	3.21	35.0	12.00	45.0
2.09	29			12.20	50.0

It took 35.6 ml of NaOH to neutralize 40.0 ml of H_2SO_4; thus the acid is less concentrated than the NaOH and its normality is:

$\frac{35.6}{40.0} \times 0.498 = .433$ N of the H_2SO_4

Plotting the above data results in a significantly differently shaped curve than when a weak acid (potassium acid phthalate) was used for standardizing the NaOH solution. The reason for this difference will be explained later.

Figure I - (page 148-a)

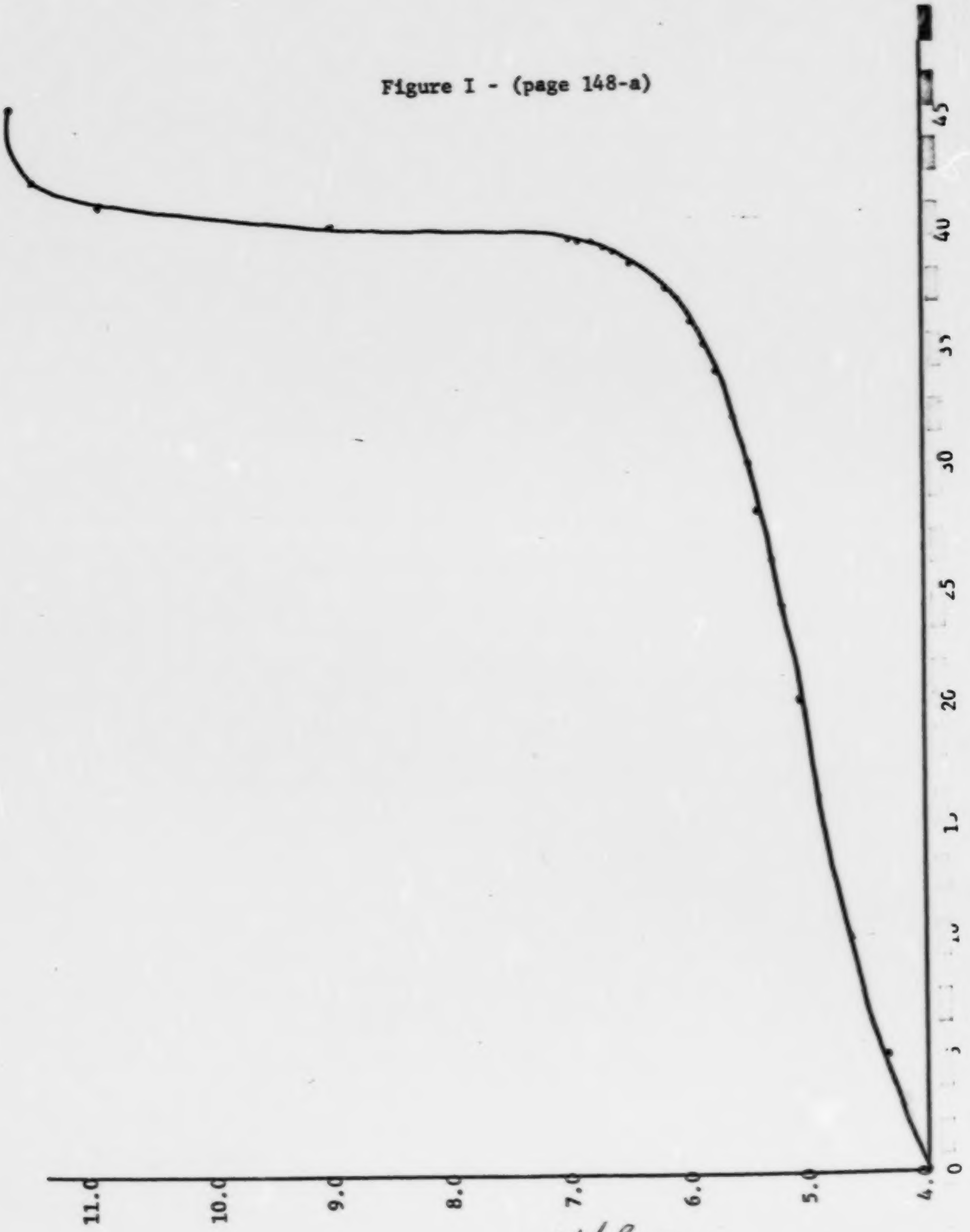
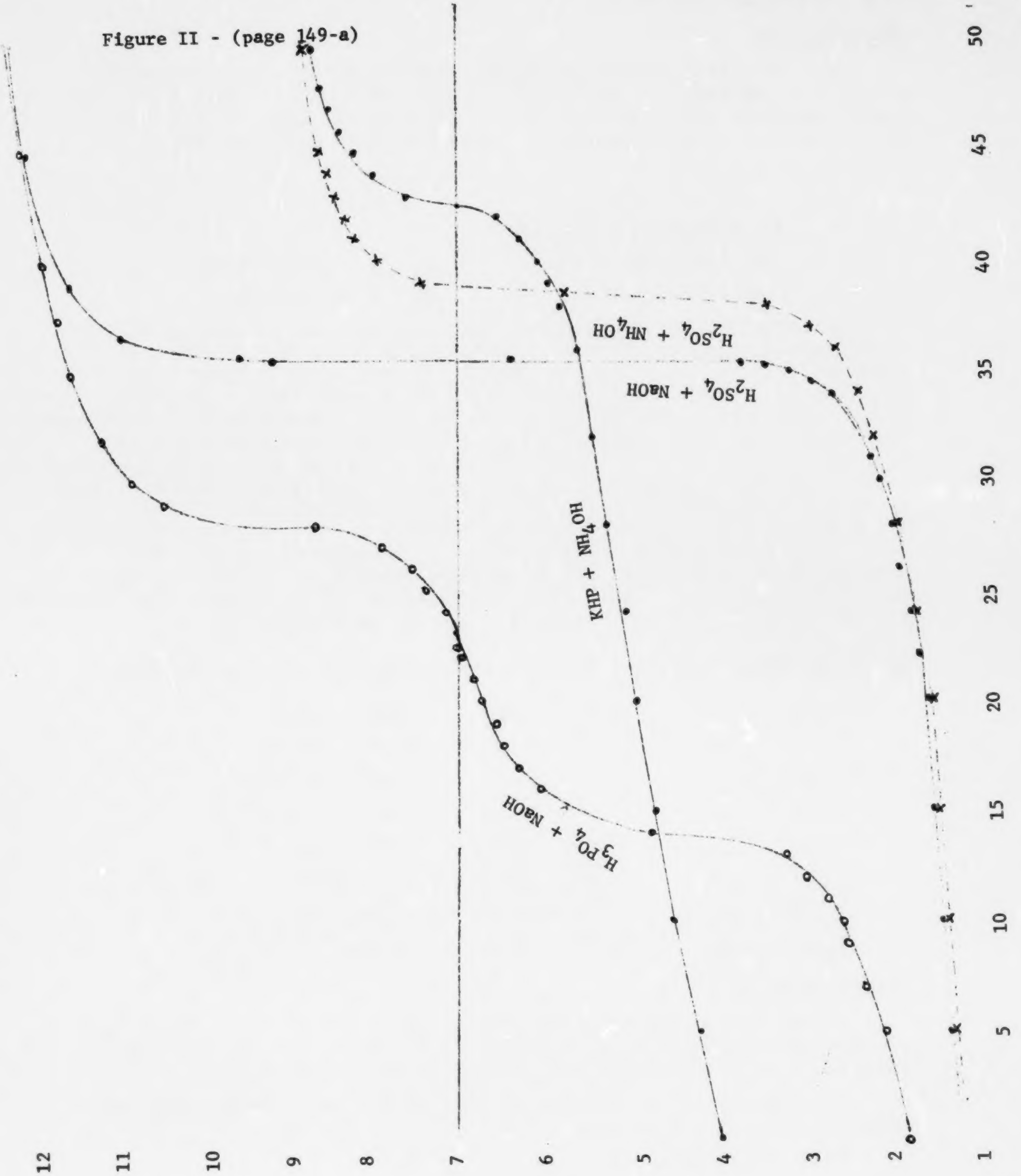


Figure II - (page 149-a)



148-b

Weak acids and bases

Exercise 13

A. Another sample of H_2SO_4 was prepared which contained about 0.4 equivalent per liter. When 50.0 ml of this were titrated against the standard NaOH, 25.3 ml of the 0.498 N were required for neutralization. What is the pH of the acid?

B. As a brief review list:

(a) 3 strong acids	(c) 2 strong bases
(b) 1 weak acid	(d) 1 weak base

It was previously stated that aqueous solutions of HCl and H_2SO_4 are strong acids - and NaOH and KOH are strong bases - because they really ionize 100%. It was also stated that CH_3COOH is a weak acid - and NH_4OH is a weak base - because of relatively low % ionization. Whereas all strong acids and bases are virtually 100% ionized, very little of the weak ones are ionized. This does not mean, however, that a weak base requires less acid for neutralization, or that a weak acid requires less base for neutralization. It does mean that as the H^+ are neutralized by the base, more of them are immediately produced by the unionized acetic acid. A 0.5 N solution of NH_4OH was standardized against: (a) a weighed amount of potassium acid phthalate and (b) a measured amount of 0.443 N H_2SO_4. The results are as follows and the data is plotted on Figure II.

NH_4OH titrated against 4.0100g. of potassium acid phthalate

pH	ml	pH	ml	pH	ml
3.95	0	5.42	32.0	6.61	42.0
4.23	5	5.53	34.0	7.00	42.6
4.51	10	5.69	36.0	7.37	43.0
4.73	15	5.85	38.0	7.99	44.0
4.93	20	5.97	39.0	8.20	45.0
5.09	24	6.10	40.0	8.38	46.0
5.24	28	6.31	41.0	8.50	47.0

Exercise 14

Using the above as a guide, prepare a 0.25 N of NH_4OH and standardize it against a standard solution of H_2SO_4 and also against a weighed amount of potassium acid phthalate.

Calculate the normality of the NH_4OH using both sets of data and compare results.

Plot your data.

Compare to Figure II.

(a) From the above, it took 42.6 ml of NH_4OH to neutralize 4.0100g. KHP (abbreviation for potassium acid phthalate)

$\frac{4.0100}{42.6} \times 1000 = 94.2$ KHP required to neutralize 1 liter of the NH_4OH

Normality of NH_4OH $= \frac{94.2}{204.22} = 0.461$ N

(b) It required 39.2 ml of the NH_4OH to neutralize 40.0 ml of 0.443 N H_2SO_4

Normality of NH_4OH $= \frac{40.0}{39.2} \times 0.443 = 0.450$ N

These are not good checks, except that it is not good practice to standardize a weak acid against a weak base. Therefore, method (b) probably gives a better figure.

ANSWERS

Pretest:

1. c - pH = 4
2. b - $[H^+] = 10^{-10}$
3. d - $[OH^-] = 10^{-11}$
4. a - $\frac{60}{1}$
5. a - 1 N
6. e - N x ml = N x ml
   .125 x 20 = N x 25
   N = .10
7. e - 20 ml HCl ppt. 0.4298g AgCl
   50 x 0.4298 = 21.49g. AgCl
   would be ppt. by 1 l. of the
   HCl equiv. wt. of AgCl. = 149.32

   143.32 : 1 :: 21.49 : x
   x = 0.15 N
8. d - 50 x 0.6126 = 30.63g. KHP
   that would be neutralized
   by 1 liter of the KOH

   204.2 : 1 :: 30.63 : x
   x = 0.15 N
9. f
10. d

ANSWERS

1.

$[H^+]$	$[OH^-]$	K_w	pH
10^{-5}	10^{-9}	10^{-14}	5
10^{-4}	10^{-10}	10^{-14}	4
10^{-3}	10^{-11}	10^{-14}	3
10^{-2}	10^{-12}	10^{-14}	2
10^{-1}	10^{-11}	10^{-14}	1
10^{-6}	10^{-8}	10^{-14}	6

2.

HCl			H_2SO_4		
g/1	moles	$[H^+]$	g/1	moles	$[H^+]$
73.0	2	2	49.0	0.5	1.0
3.65	0.1	0.1	.49	.005	0.01
.0365	0.001	0.001	98	1.0	2.0
.183	0.05	0.05	.0245	0.00025	0.0005

3. Normality same as $[H^+]$ above.

4. A. 1 liter of I N HNO_3 requires 73g HNO_3

$V = \frac{m}{d} = \frac{73}{1.42} = 51.4$ ml of 100% HNO_3

$\frac{51.4}{.70} = 73.5$ ml of stock HNO_3

B. 1 liter of 0.1 N H_3PO_4 requires

0.1 x 98 x 1/3 = 3.3g of 100% H_3PO_4

$V = \frac{m}{d} = \frac{3.3}{1.73} = 1.91$ ml of 100% H_3PO_4

$\frac{1.91}{.85} = 2.3$ ml of stock H_3PO_4

C. 1 liter of 0.5 N CH_3COOH requires

0.5 x 60 = 30.0g. of 100% CH_3COOH

$V = \frac{m}{O} = \frac{30.0}{1.07} = 28.0$ ml of 100% CH_3COOH

$\frac{28.0}{.98} = 29.0$ ml of stock CH_3COOH

5.

	NH_4OH
Mol wt.	35
Density	.90
Assay	29%

6. The assay of stock solutions vary, as noted on the labels. Therefore, it is futile to try to measure the volumes with great accuracy; thus a graduated cylinder is used.

7. A. $Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$

B. $3Ca(OH)_2 + 2H_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6H_2O$

C. $HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$

D. $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$

8. As stated in a previous Study Guide, there are three driving forces that may cause a chemical reaction to proceed, and precipitation is one of them.

9. $40.0 \times 0.513 = 45.6 \times X$

$$X = \frac{40.0 \times 0.513}{45.6} = 0.450 \text{ N of } H_2SO_4$$

10. $\frac{7.5578}{45.2} \times 1000 = 167.2$g. of potassium acid phthalate would be required to neutralize 1 1. of the KOH solution.

$\frac{167.2}{204.22} = 0.819$ N, normality of the KOH solution.

11. $0.490 \times \frac{32.2}{25.0} = 0.623$ N.

13. A. $30.0 \times X = .498 \times 25.3$

$$X = \frac{.498 \times 25.3}{30.0} = .420 \text{ N of } H_2SO_4$$

This means the solution of H_2SO_4 produces: $[H^+] = .420$ mols/1

$$pH = -\log [H^+]$$
$$pH = -\log .420 = -\log (4.20 \times 10^{-1})$$
$$pH = -[.62 + (-1)] = .38$$

B. a.) HCl, H_2SO_4, HNO_3

b.) CH_3COOH

c.) KOH, NaOH

d.) NH_4OH

BUFFERS

SUMMARY

The measurement of pH, a thorough understanding of acids and bases, and many of the principles yet to come, depend upon working with solutions of carefully adjusted hydrogen ion concentration. Buffers are often an essential part of such adjustments. The concept of the Debye-Huckel Theory is also included in this mini-course as a means of calculation buffer solutions more accurately than can be done if only the concentrations of the solutions are considered.

ACKNOWLEDGEMENTS

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PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. State what is meant by molar and normal concentrations.
2. Interconvert between weight, volume, and either M or N, when given any two of these and the formula for a compound.
3. Use exponents and logarithms.
4. Interconvert between pH, H^+, and OH^-.
5. Define neutralization and do a titration.
6. Use equilibrium constants to calculate the concentration of the equilibrium species when given the concentration of one or more of these.

OBJECTIVES

At the completion of this mini-course, the student should be able to:

1. Define what is meant by a buffer and describe how a buffer keeps the pH relatively constant.
2. Given a weak acid or base and its salt, calculate the pH of a buffer solution using the ionization product constant.
3. Use the Debye-Huckel Theory to calculate a more exact pH than found from simple concentration calculations.
4. Perform a titration with weak acid and/or base and verify the calculated pH at each step using the buffer calculations.
5. Use a buffered solution to standardize a pH meter.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. What would be the pH of a 0.005 M solution of NaOH?

2. When 10 ml of a 0.5 M solution of HCl is diluted to 200 ml, what would be the pH?

3. A solution contains 0.05 $HC_2H_3O_2$ and 0.10 M $NaC_2H_3O_2$. What would be the pH? ($K = 1.8 \times 10^{-5}$ for $HC_2H_3O_2$).

4. How many moles of NH_4Cl must be added to 0.5 liter of 0.1 M NH_4OH to give a pH of 10.2? (K for $NH_4OH = 1.8 \times 10^{-5}$).

5. During a titration, a 100 ml sample of 0.10 M NH_4OH has added to 50 ml of 0.10 M HCl. Calculate the pH. (K for $NH_4OH = 1.8 \times 10^{-5}$).

6. Use the Debye-Huckle Theory to calculate the pH of a solution containing 0.01 mole of NH_4OH and 0.01 M NH_4Cl. Compare this to the answer expected for simple concentration calculations.

BUFFERS

The measurement and adjustment of pH is one of the easiest, fastest and most important measurements made by the water chemist. Raising or lowering the pH can lessen the solubility of many undesirable ions and thus facilitate water purification. High or low pH readings tell much regarding the condition of raw water and what must be done to correct the condition. Buffers help the chemist to measure and control pH.

In general, buffers are used to (1) stabilize the pH of aqueous solutions or (2) standardize a pH meter. The former will be utilized in many of the analyses run on water samples; we will now be concerned with the way buffers stabilize the pH of aqueous solutions.

Suppose that 1 ml of 1.0 N HCl were added to 1 liter of distilled water:

1 ml of 1.0 N HCl/liter = 0.001 x 1.0 = 0.001 equivalents of H^+/liter.

Thus, the $[H^+] = 10^{-3}$, pH = 3.0

Exercise 1

What would be the pH of a solution which contains 2 ml of 1.0 N HCl in 500 ml of solution?

So it is that large changes in the pH of water are caused by the addition of small amounts of strong acids. The purpose of a buffer is to minimize these changes.

Our study of acids and bases laid the foundation for understanding the role of buffers. A review of the titration curves when a strong base was added to a weak acid, or a strong acid was added to a weak base, shows that the curve is quite flat at the mid-way point. That is, the pH is changing very little when half the weak base has been neutralized:

$$NH_4OH \longrightarrow NH_4^+ + OH^-$$

$$K_d = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

Suppose that a 0.1 M solution of NH_4OH were half neutralized with HCl. At the mid-way point, half the NH_4OH has been converted into NH_4Cl - which is completely ionized since it is a salt. Therefore:

$[NH_4^+] = [NH_4OH]$ and the above equation becomes:

$$K_d = \frac{[NH_4^+][OH]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

Since $[NH_4^+] = [NH_4OH]$, then

$$[OH^-] = 1.8 \times 10^{-5}$$

$$[H^+] = 5.55 \times 10^{-10}, \ pH = 9.26$$

Next, taking different concentrations of NH_4^+ and NH_4OH, the pH can be calculated. For example, what would be the pH of a solution which is 0.2 in NH_4OH and 0.05 M in NH_4Cl?

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

$$\frac{[.05][OH^-]}{[.2]} = 1.8 \times 10^{-5}$$

$$[OH^-] = 7.2 \times 10^{-5}$$

$$[H^+] = 1.4 \times 10^{-10}, \ pH = 9.86$$

Exercise 2

What would be the concentration of NH_4OH if 100 ml of 0.100 M solution of it were 1/3 neutralized with 0.100 M HCl?

(Note: the solutions are diluted upon mixing.)

Exercise 3

What would be the concentration of NH_4^+ in Exercise 2 after the NH_4OH is 1/3 neutralized?

Exercise 4

What would be the $[OH^-]$ in Exercise 2 after the NH_4OH is 1/3 neutralized?

Exercise 5

What is the $[H^+]$ in Exercise 4?

Exercise 6

What is the pH in Exercise 5?

Now let us see what would happen if 1 ml of 1.0 N HCl were added to 1 liter of the above solution. This is still 0.001 equivalents of H^+ per liter so that the $[NH_4OH]$ is reduced by 0.001 and the $[NH_4^+]$ is increased by the same amount.

Exercise 7

What are the new concentrations of $[NH_4^+]$ and $[NH_4OH]$?

Exercise 8

What is the final pH of this solution?

Thus:

$$K_d = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{(0.025 + 0.001)[OH^-]}{(0.05 - 0.001)} = 1.8 \times 10^{-5}$$

$$[OH^-] = 1.8 \times 10^{-5} \times \frac{0.026}{0.051} = 1.73 \times 10^{-5}$$

$$[H^+] = 5.77 \times 10^{-10}, \text{ pH} = 9.54$$

Thus the addition of 1 ml of 1.0 HCl to the above solution changed the pH from 9.56 to 9.54, a difference that can be barely detected by a good pH meter. Without the buffer the pH changed from 7.0 to 3.0. (See page

The student should note that a buffer stabilized the pH of the solution at or near the logarithm of the $[H^+]$ of the dissociation constant. Thus equal molar concentrations of NH_4Cl and NH_4OH (say 0.1 M each) result in a buffer whose pH = 9.26. That this is not exactly so will be developed on a later page.

Exercise 9

What would be the change in pH if 2.0 ml of 1.0 N HCl were added to 100 ml of a buffer solution made of 0.10 mole of NH_4Cl and 0.10 mole of NH_4OH dissolved in 1 liter of distilled water?

An acidic buffer is made by starting with a weak acid such as acetic acid. If a 0.1 M solution of this is half neutralized with 0.1 M NaOH, then the $[Ac^-] = [HAc]$ and the equilibrium equation becomes:

$$HAc \quad [H^+]+[Ac^-]$$

$$K_d = \frac{[H^+][Ac^-]}{HAc} = 1.8 \times 10^{-5}$$

$$[Ac^-] = [HAc] = 0.0500 \times \frac{100 \text{ ml}}{150 \text{ ml}} = .033 \text{ M}$$

$$\frac{[H^+]\ (0.033)}{(0.033)} = 1.8 \times 10^{-5}$$

$$[H^+] = 1.8 \times 10^{-5}, \ pH = 4.75$$

Let us now add 1 ml of 0.1 N NaOH to a liter of the above solution. For the same reason as given above, the amount of NaOH equals 0.001 equivalents of OH^- per liter.

Exercise 10

What are the concentrations of HAc and Ac^- after adding the NaOH?

Exercise 11

What is the final pH of the solution?

The addition of 1 ml of 1.0 N NaOH to 1 liter of the above solution has thus changed the pH from 4.75 to 4.76.

When standardizing a pH meter, buffers should be used which give a pH close to the value of the sample being tested. In the above, we have seen how to prepare acidic and basic buffers whose pH is stabilized above and below the neutral point, specifically at pH = 9.26 and 4.75. How would you prepare a buffer that is (a) more acidic and (b) more basic than the above, and (c) neutral?

The dissociation constants for the following compounds are:

Compound	K_d
H_3PO_4	7.5×10^{-3}
$NaHCO_3$	4.7×10^{-11}
KH_2PO_4	6.2×10^{-8}

If, in each of the above cases, 0.1 M solutions of these compounds were prepared and then half neutralized with a strong base or acid, the pH of the resulting solutions could be calculated.

Exercise 12

What would be the pH of the solution resulting from the half neutralization of 0.1 M H_3PO_4?

NOTE: $H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$

$$K_d = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

Exercise 13

What would be the pH of the solution resulting from the half neutralization of 0.1 M $NaHCO_3$ with 0.1 M NaOH?

Exercise 14

What would be the pH of the solution resulting from the half neutralization of 0.1 M KH_2PO_4 with 0.1 M NaOH?

Two matters of importance remain unanswered:

1. In relatively concentrated solutions, the pH of buffers made from the weak acids and weak bases used above does not exactly equal the experimental results. Can this be corrected?
2. Using a phosphate system, a pH = 7.21 comes

close to neutrality. How can a buffer of exactly pH = 7.0 be prepared?

The Debye and Huckel Theory

It has been stated a number of times that almost all salts are completely ionized. This means that in the case of:

$$K_2HPO_4 \longrightarrow 2K^+ + HPO_4^{--}$$

there is no un-ionized K_2HPO_4.

Other tests, such as freezing point lowering, indicate that such salt solutions do have strong interionic attractions which make them appear to be less than 100% ionized, especially in concentrated solutions. Why the seeming discrepancy? Chemists offer the following explanation.

The plight of an ion in water is analogous to a person trying to push through a crowd, or a football player running for a touchdown with part of the opposing team hanging on his back. The positively charged K^+ is surrounded by negatively charged HPO_4^{-2} which inhibit the freedom of its motion; even other K^+ ions tend to block its path - much like a team-mate getting in the way of the runner. Finally, water molecules themselves surround and cling to the charged ions - both poitive and negative - thus forming what is called hydrated ions. The overall effect is that the activity of the ion is less than the concentration predicts that it should be.

The correction factor is called the "activity coefficient"; it is a number less than one that, when multiplied by the concentration, gives the activity of the ion - or its effective concentration. Let -

c = concentration

y = activity coefficient

a = activity

Electrochemistry provides a way of experimentally determining activity coefficients. This will be developed later.

The Debye and Huckel theory permits the calculation of activity coefficients; agreement with experimental results is fairly good for solutions less concentrated that 0.1 M. The derivation of the Debye and Huckel theory is beyond the scope of this course, but that does not prevent its use because the formula and the procedure for using it is fairly simple. Actually, many mathematical expressions that we use are not derived:

$F = ma$, force = mass x acceleration

$E = q - w$, internal energy = heat - work

So let us apply the Debye and Huckel theory without derivation to the following chemical equation, since this is the basis for preparing a buffer that is close to the neutral point.

$$H_2PO_4^- \longrightarrow H^+ + HPO_4^{--}$$

$$K_d = 6.2 \times 10^{-8} = \frac{[H^+][HPO_4^{--}]}{[H_2PO_4^-]}$$

$$[H^+] = 6.2 \times 10^{-8} \times \frac{[H_2PO_4^-]}{[HPO_4^{--}]}$$

Following the procedure used earlier in this study guide, we next want to have equal molar amounts of $H_2PO_4^-$ and HPO_4^{--}. These can be obtained most readily by using KH_2PO_4 and K_2HPO_4 - say 0.01 moles of each:

$$KH_2PO_4 \longrightarrow K^+ + H_2PO_4^-$$

$$K_2HPO_4 \longrightarrow 2K^+ + HPO_4^{--}$$

The Debye and Huckel theory defines and uses the following terms:

u = ionic strength

Z = charge of the ion

a = activity

$u = 1/2 \Sigma cZ^2$, the symbol Σ means "the summation of".

In words this says that the ionic strength is 1/2 the summation of the individual concentrations multiplied by the square of the charge on each ion.

Let us now take a solution of 0.010 M KH_2PO_4 and 0.010 M K_2HPO_4.

Exercise 15

What would be the molar concentration of the following ions?

K^+

$H_2PO_4^-$

HPO_4^{--}

Exercise 16

What are the charges on the above ions?

Exercise 17

What are the values of cZ^2 for each of the above ions and what is the value of $\Sigma\ cZ^2$?

Exercise 18

What is the ionic strength (u) of this solution?

The formula for the activity coefficient (y) is given as:

$$\log y = -0.5 \Sigma Z^2 \frac{\sqrt{u}}{1 + \sqrt{u}}$$

Exercise 19

What is the activity coefficient of a +1 charged ion having an ionic strength of 0.01?

Exercise 20

What is the activity coefficient of a -1 charged ion having an ionic strength of 0.01?

You have seen that it doesn't make any difference whether an ion has a +1 or a -1 charge, since the Z term is squared.

Exercise 21

What is the activity coefficient for K^+ and/or $H_2PO_4^-$ in Exercise 18?

Exercise 22

What is the activity coefficient for HPO_4^{--} in Exercise 18?

Remember a = cy (activity = concentration x activity coefficient.)

$$[H^+] = 6.2 \times 10^{-8} \times \frac{[H_2PO_4^-]}{[HPO_4^{--}]} \text{ for reaction being studied}$$

$$[H^+] = 6.2 \times 10^{-8} \times \frac{\text{activity of } H_2PO_4^-}{\text{activity of } HPO_4^{--}}$$

Exercise 23

What is the pH of the solution being studied, using concentration rather than activities?

Exercise 24

What is the pH of the solution being studied, using activities?

Notice that the activity coefficient makes a considerable difference in the calculated pH.

Substituting these values in the equilibrium equation for the phosphate system, remembering that a = c x y.

$$[H^+] = 6.2 \times 10^{-8} \times \frac{[H_2PO_4^-]y}{[HPO_4^{--}]y}$$

$$[H^+] = 6.2 \times 10^{-8} \times \frac{0.830 \times 0.01}{0.464 \times 0.01} = 1.1 \times 10^{-7}, \text{ pH} = 6.94$$

Thus when a solution of equal molar concentrations of KH_2PO_4 and K_2HPO_4 are prepared, the buffer solution should have a pH = 6.94, and it does. In other words, calculations based on the effective concentration - which by definition is the activity - predicted that equal amounts of these two phosphate solutions should have a pH = 6.94. This can be verified.

Since it is more convenient to use concentrations than activities, the above equation can be written as:

$$H^+ = 1.1 \times 10^{-7} \times \frac{[H_2PO_4^-]}{[HPO_4^{--}]}$$

Replacing the constant 6.2×10^{-8} with 1.1×10^{-7} is another way - and a simpler way - of converting concentrations into activities. Obviously the activities must be calculated in the first place, before this substitution can be made.

Now to answer the second question: using a phosphate system, how can we prepare a buffer solution of exactly pH = 7.0? In other words, we want the $[H^+] = 1.0 \times 10^{-7}$ in the above equation.

Thus:

$$1 \times 10^{-7} = 1.1 \times 10^{-7} \times \frac{[H_2PO_4^{-}]}{[HPO_4^{--}]}$$

$$\frac{[HPO_4^{--}]}{[H_2PO_4^{-}]} = \frac{1.1 \times 10^{-7}}{1.0 \times 10^{-7}} = 1.1$$

Therefore a solution containing 0.011 moles of K_2HPO_4 plus 0.010 moles of KH_2PO_4 should give a buffer whose pH = 7.0 - and it does.

The Debye and Huckel theory does not result in good agreement with more concentrated solutions, so:

Exercise 25

By experiment, using 0.1 M solutions, determine the ratio of K_2HPO_4/KH_2PO_4 required to make a buffer of pH = 7.0. How does this agree with the Debye-Huckel theory?

Exercise 26

What is the H^+ concentration of a 0.01 M NH_4Cl, 0.01 M NH_4OH system? Use the Debye-Huckel theory. Check your answer against an experimental pH determination.

Exercise 27

What is the ratio of NH_4Cl/NH_4OH needed to give a buffer whose pH = 9.0? (Use the results from Exercise 26.)

Exercise 28

What is the hydrogen-ion concentration of a solution containing 1/10 mole of acedic acid plus 1/10 mole of sodium acetate?

Exercise 29

What is the ratio of sodium acetate/acetic acid needed to give a buffer whose pH = 5.0? (Use the results from Exercise 28).

ANSWERS

A. Pretest

1. 11.7
2. 1.6
3. 5.05
4. 0.0055 mole of NH_4Cl
5. 9.26
6. 9.30 The simple calculation gives pH = 9.26, so ionic attractions make the difference.

B. Study Guide

Exercise 1

2 ml = 0.002 1 = 0.002 equivalents of H^+ added to 500 ml.

= 0.004 moles H^+ per liter.

$[H^+] = 1 \times 10^{-3}$

$pH = -\log [H^+] = -(-3)$

$pH = 3$

Exercise 2

$[NH_4OH] = 0.100$ M

1/3 is neutralized $\quad 1/3\ (0.100) \times \dfrac{100 \text{ ml}}{133 \text{ ml total}} =$

$.025 \text{ M} = [NH_4^+]$

2/3 remains unchanged $= 2/3(0.100)\dfrac{(100)}{(133)} = .050 \text{ M} = [NH_4OH]$

$[NH_4OH] = 0.050$ after being 1/3 neutralized. The solution was diluted from 100 ml to 133 ml by addition of the HCl.

Exercise 3

From Exercise 2 since 1/3 is neutralized this 1/3 becomes NH_4^+ and is diluted also.

$(NH_4OH + HCl \longrightarrow NH_4Cl + H_2O)$

$[NH_4^+] = 0.025$ M (See the Answer to Exercise 2).

Exercise 4

We do not know the $[OH^-]$ and therefore assign it a value of X.

Since $K_d = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$

Then $[OH^-] = \dfrac{1.8 \times 10^{-5}\ [NH_4OH]}{NH_4^+}$

$[OH^-] = \dfrac{1.8 \times 10^{-5}\ [.050]}{.025}$

$$[OH^-] = 3.6 \times 10^{-5}$$

Exercise 5

Since $[H^+][OH^-] = 1 \times 10^{-14}$

$$[H^+] = \frac{1 \times 10^{-14}}{[OH^-]} = \frac{1 \times 10^{-14}}{3.6 \times 10^{-5}} = 0.278 \times 10^{-9}$$

$$[H^+] = 2.78 \times 10^{-10}$$

Exercise 6

$$pH = -\log [H^+] = -\log 2.78 \times 10^{-10}$$

$$pH = -(10 + \log 2.78)$$

$$pH = (10 - 0.44)$$

$$pH = 9.56$$

Exercise 7

$[NH_4^+]$ was $[0.025]$ and was increased by 0.001.

$$[NH_4^+] = [0.025 + 0.001] = 0.026$$

$$[NH_4^+] = 0.026 \text{ M}$$

$[NH_4OH]$ was $[0.05]$ and was decreased by 0.001.

$$[NH_4OH] = [0.050 - 0.001] = [0.049]$$

$$[NH_4OH] = 0.049 \text{ M}$$

Exercise 8

$$[OH^-] = \frac{(1.8 \times 10^{-5}) \quad NH_4OH}{[NH_4^+]}$$

$$[OH^-] = \frac{(1.8 \times 10^{-5}) \quad 0.049}{[.026]}$$

$$[OH^-] = 3.4 \times 10^{-5}$$

$$[H^+] = 2.9 \times 10^{-10}$$

$$pH = 9.54$$

Exercise 9

Initially, $[NH_4^+] = 0.100$

$[NH_4OH] = 0.100$

If we add 2.00 ml of 0.1000 N HCl we have added 0.002 x 0.100 = 0.0002 equivalents of H^+ and thus decreased NH_4OH by 0.0002 and increased NH_4^+ by 0.0002.

Finally $[NH_4^+] = 0.1000 + 0.0002 = 0.1002$

$[NH_4OH] = 0.1000 - 0.0002 = 0.0998$

Initially $[OH^-] = \frac{1.8 \times 10^{-5}[NH_4OH]}{[NH_4^+]} = \frac{1.8 \times 10^{-5} \times 0.1000}{0.1000}$

$[OH^-] = 1.8 \times 10^{-5}$

$[H^+] = 5.55 \times 10^{-10}$

$pH = 9.26$

Finally $[OH^-] = 1.8 \times 10^{-5} \times \frac{0.0098}{0.1002}$

$[OH^-] = 1.8 \times 10^{-5} \times (0.9960)$

$[OH^-] = 1.793 \times 10^{-5}$

$[H^+] = 5.58 \times 10^{-10}$

$pH = 9.25$

Exercise 10

$[HAc]$ is decreased by 0.001 and the $[Ac^-]$ increased by 0.001

$[HAc] = (0.033 - 0.001) = 0.032$

$[Ac^-] = (0.033 + 0.001) = 0.034$

Exercise 11

$[H^+] = 1.8 \times 10^{-5} \times \frac{0.032}{0.034} = 1.73 \times 10^{-5}$

$pH = 4.76$

Exercise 12

$H_3PO_4 \longrightarrow H^+ + H_2PO_4^{--}$

$K_d = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^{--}]}{[H_3PO_4]}$

$\frac{[H^+] \times (0.033)}{(0.033)} = 7.5 \times 10^{-3}$

$[H^+] = 7.5 \times 10^{-3}$, $pH = 2.13$

Exercise 13

$NaHCO_3 \longrightarrow H^+ + CO_3^{--}$

$K_d = 4.7 \times 10^{-11} = \frac{[H^+][CO_3^{--}]}{[NaHCO_3]}$

$\frac{[H^+]\ (0.033)}{(0.033)} = 4.7 \times 10^{-11}$

$[H^+] = 4.7 \times 10^{-11}$, $pH = 10.32$

Exercise 14

$H_2PO_4^- \longrightarrow H^+ + HPO_4^{--}$

$K_d = 6.2 \times 10^{-8} = \frac{[H^+][HPO_4^{--}]}{[H_2PO_4^-]}$

$\frac{[H^+]\ (0.033)}{(0.033)} = 6.2 \times 10^{-8}$, pH = 7.21

Exercise 15

$[K^+] = 0.010$ M from KH_2PO_4

$+0.020$ M from K_2HPO_4*

*Note $K_2HPO_4 \longrightarrow \underline{\underline{2K^+}} + HPO_4^{--}$

$[H_2PO_4^-] = 0.010$ M from KH_2PO_4 only

$[HPO_4^{--}] = 0.010$ M from K_2HPO_4 only

Exercise 16

Ion	Z
K^+	+1
$H_2PO_4^-$	-1
HPO_4^{--}	-2

Exercise 17

Ion	c	Z	cZ^2
K^+	0.03	+1	0.03
$H_2PO_4^-$	0.01	-1	0.01
HPO_4^{--}	0.01	-2	0.04
		$\Sigma\ cZ^2 =$	0.08

Exercise 18

M = 1/2 $\quad cZ^2 = 0.04$

M = 0.04

Exercise 19

$\log y = -0.5\ (+1)^2 \frac{\sqrt{0.01}}{1 + \sqrt{0.01}}$

$\log y = -.5 \times \frac{(.1)}{1.1}$

$\log y = -0.046 = -1 + .954$

$y = 0.900$

Exercise 20

$$\log y = -0.5(-1)^2 \quad x \quad \frac{\sqrt{0.01}}{1 + \sqrt{0.01}}$$

$$\log y = -0.5(1) \quad x \quad \frac{\sqrt{0.01}}{1+ \sqrt{0.01}}$$

$$y = 0.900$$

Exercise 21

$$\log y = -0.5\ Z^2 \ x \ \frac{\sqrt{u}}{1 + \sqrt{u}}$$

for K^+ or $H_2PO_4^-$ $\quad \log y = -0.5(\pm 1) \ x \ \frac{\sqrt{0.04}}{1 + \sqrt{0.04}}$

$$\log y = -0.0833$$

$y = 0.825$ for singly charged ions

Exercise 22

$$\log y = -0.5(-2)^2 \ \frac{0.04}{1 + \quad 0.04}$$

$$\log y = -0.333$$

$y = 0.464$ for doubly charged ions

Exercise 23

$$[H^+] = 6.2 \times 10^{-8} \ \frac{[H_2PO_4^-]}{[HPO_4^{--}]}$$

$$[H^+] = 6.2 \times 10^{-8} \ \frac{[0.01]}{[0.01]}$$

$$[H^+] = 6.2 \times 10^{-8}$$

$$pH = 7.21$$

Exercise 24

$$[H^+] = 6.2 \times 10^{-8} \times \frac{[0.830 \times 0.01]}{[0.464 \times 0.01]}$$

$$[H^+] = 1.1 \times 10^{-7}$$

$$pH = 6.94$$

Exercise 25

Experimental

(a) Zero pH meter using a standard pH = 7 buffer.

(b) Place 50 ml of 0.1 M K_2HPO_4 solution in a beaker.

(c) Put electrodes in solution and record pH.

(d) Slowly add 0.1 M KH_2PO_4 solution from a burette until pH reads 7.0. Record the volume of KH_2PO_4 solution used.

(e) Calculate the number of moles of KH_2PO_4 added and the number of moles of K_2HPO_4 already present.

(f) Divide each by the total volume in liters M/1.

(g) Using the Debye-Huckel theory, calculate the expected pH.

(h) Compare experimental and calculated results.

Exercise 26

$$[OH^-] = \frac{1.8 \times 10^{-5}\,[NH_4OH]}{[NH_4^+]}$$

Ion	c	Z	cZ^2
NH_4^+	0.01	+1	0.01
Cl^-	0.01	-1	0.01
NH_4OH	0.01	0	0

$$\Sigma\, cZ^2 = 0.02$$

$$u = 1/2\ \Sigma\, cZ^2 = 0.01$$

$$\log y = \frac{-0.5(+1)^2\ \sqrt{0.01}}{1 + \sqrt{0.01}}$$

same as Exercises 19 and 20

$$y = 0.900$$

$$[OH^-] = \frac{1.8 \times 10^{-5}\,[0.01]}{(0.900)(0.01)}$$

$$[OH^-] = 2 \times 10^{-5}$$

$$[H^+] = \frac{1 \times 10^{-14}}{2 \times 10^{-5}} = 0.5 \times 10^{-9} = 5 \times 10^{-10}$$

$$[H^+] = 5 \times 10^{-10}$$

Exercise 27

$$pH = 9.0$$

$$[H^+] = 1 \times 10^{-9}$$

$$[OH^-] = 1 \times 10^{-5}$$

$$[OH^-] = \frac{1.8 \times 10^{-5}}{0.900} \times \frac{NH_4OH}{NH_4Cl}$$

$$\frac{NH_4Cl}{NH_4OH} = \frac{1.8 \times 10^{-5}}{0.900} \times \frac{1}{1 \times 10^{-5}}$$

$$\frac{NH_4Cl}{NH_4OH} = 2 \text{ or } 2/1$$

Exercise 28

$$[H^+] = K_d \frac{[HAc]}{[Ac^-]}$$

$$[H^+] = 1.8 \times 10^{-5} \frac{[HAc]}{[Ac^-]}$$

Ion	c	Z	cZ^2
HAc	0.1	0	0
H^+	0.1	+1	0.1
Ac^-	0.1	-1	0.1
			0.2

$M = 1/2 \quad cZ^2 = 0.1$

$M = 0.1$

$$\log y = \frac{-0.5(1)^2 \sqrt{0.1}}{1 + \sqrt{0.1}} = \frac{-0.5 \sqrt{0.1}}{1 + \sqrt{0.1}} = \frac{-0.5(.32)}{1.32}$$

$\log y = -0.120 = -1 + .879$

$y = 0.758$

$$[H^+] = 1.8 \times 10^{-5} \times \frac{0.1}{(0.758)(0.1)}$$

$$[H^+] = 2.37 \times 10^{-5}$$

Exercise 29

$pH = 5.0$

$[H^+] = 1 \times 10^{-5}$

$$[H^+] = 1.8 \times 10^{-5} \frac{[HAc]}{[Ac^-]}$$

$$[Ac^-] = \frac{1.8 \times 10^{-5}}{[H^+]} = \frac{1.8 \times 10^{-5}}{1 \times 10^{-5}}$$

$$\frac{[Ac^-]}{[HAc]} = 1.8$$

OXIDATION-REDUCTION REACTIONS

SUMMARY

In this mini-course the concepts of valence and oxidation states are reviewed and used to balance complex oxidation-reduction equations. The half-reaction method of balancing redox equations is used.

RATIONALE

Many of the most critical analyses made by the water chemist involve oxidation-reduction reactions. Even though a course in introductory chemistry includes this subject, it is essential that the student review this material and particularly as it applies to the analysis of water.

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PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. Use the periodic chart to identify the oxidation states of the "regular" elements, such as:

Group I-A = +1
Group II-A = +2
Group III-A = +3 (sometimes +1)
Group IV-A = +4 (sometimes +2 and -4)
Group V-A = +5, +3, -3
Group VI-A = -2, +6, +4
Group VII-A = -1, +7, +5 (and others)

2. State that any uncombined element has an oxidation state = 0.

OBJECTIVES

At the completion of this mini-course, the student should be able to:

1. Using the periodic chart, state the valence of the key elements in the Periodic Table.
2. Define valence and oxidation numbers.
3. Determine the oxidation number of an element in a compound using the formula of the compound and the periodic chart.
4. By looking at a chemical equation, state whether or not it is an oxidation-reduction reaction.
5. Given an equation, identify which element in a reaction is oxidized, which is reduced, which is the oxidizing agent, and which is the reducing agent.
6. Balance an oxidation-reduction reaction by balancing the gain and loss of electrons in each half reaction, then combining these to make a complete equation.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. Identify the oxidation state of each of the elements in the following compounds:

a. CaO d. H_2SO_4

b. NH_3 e. $Ca(NO_3)_2$

c. NO_2 f. FeI_2

2. Given the following equations, identify the element oxidized, the element reduced, the oxidizing agent, and the reducing agent.

a. $Fe + Cl_2 \longrightarrow FeCl_3$

b. $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

c. $PbS + HNO_3 \longrightarrow Pb(NO_3)_2 + S + H_2O + NO$

3. Balance the equations in #2.

OXIDATION-REDUCTION REACTIONS

The Study Guide on Dissociation Constants stated that a change in valence is one of the driving forces that promotes a chemical reaction. Since introductory chemistry is a prerequisite for this course, all students reading this should have previously studied oxidation-reduction reactions. Even so, experience shows that many students need repetition to drive home the importance of this Study Guide, since much of the chemistry encountered throughout the remaining Guides involves oxidation-reduction reactions in aqueous solutions.

Perhaps the most familiar oxidation-reduction reactions known to everyone - and of particular concern to the water chemist - is the rusting of iron. The prevention of rust is an expensive, troublesome and prevalent problem. The term itself - oxidation - describes what happens: metallic iron reacts with the oxygen in the air (or in water) to form iron oxide or rust.

Exercise 1

What is the chemical formula for rust?

Exercise 2

What is the balanced equation for the reaction of iron with oxygen to form iron (III) oxide?

Obviously, the rusting of iron occurs spontaneously; the flames and fury of a blast furnace testify to the difficulty of reversing this reaction and thereby converting rust into iron. (The reverse reaction of removing the oxygen from the oxide to form metallic iron is known as reduction.) In large part, iron ore is Fe_2O_3. A simplified version of what happens in a blast furnace is the reduction of Fe_2O_3 with carbon to produce free iron and carbon dioxide.

Exercise 3

What is the balanced equation for the reduction of Fe_2O_3 with carbon?

Thus - so far as the iron is concerned - the above two equations are opposite to one another. In the first case, metallic iron is oxidized to ferric oxide; in the other reaction, ferric oxide is reduced to metallic iron.

By now the thoughful student should be asking - if he doesn't already know - what precisely is meant by the term: oxidation and reduction. He does know that ferric iron has a valence of +3 and that combined oxygen has a valence of -2, and that both metallic iron and atmospheric oxygen have valences of zero. Thus the above reactions may be written:

$$2Fe^{o} + 3/2\ O_2^{\,o} \longrightarrow \overset{2(3+)}{Fe_2}\overset{3(2-)}{O_3}$$

$$3/2\ C^{o} + \overset{2(3+)}{Fe_2}\overset{3(2-)}{O_3} \longrightarrow 2Fe^{o} + 3/2\ \overset{(4+)}{C}\overset{2(2-)}{O_2}$$

Much has been packed into these equations that may not be obvious. For example, in each case there is the loss and gain of electrons; therefore, each of the above two equations can be divided into two parts, each of which is known as a half-reaction.

Iron is changed to iron (III). The answer to question two illustrates the fact that $2Fe^{o}$ are converted to $2Fe^{3+}$. In order for this to happen, the $2Fe^{o}$ must gain or lose electrons. If we had the following equation:

$$Fe^{o} \longrightarrow Fe^{3+}$$

Exercise 4

How many electrons would be needed for Fe^{o} to be converted to Fe^{3+}?

Exercise 5

Would electons be added or removed to the Fe^{o}? Explain your answer.

Now consider our immediate problem, $2Fe^{o}$ being converted to $2Fe^{3+}$.

Exercise 6

How many electrons are involved in this half-reaction, and are the electrons added or removed?

Exercise 7

What is the complete half-reaction for $2Fe^{o}$ being changed to $2Fe^{3+}$?

Notice that the oxidation number has increased (0 to 3+) and that we have lost electrons. This loss of electrons and subsequent increase in charge is an example of oxidation. Let us now consider the other half-reaction, i.e. $3/2\ O^{o}_2 \longrightarrow 3\ O^{2-}$.

Exercise 8

How many electrons are involved in this half-reaction and are they gained or lost?

Exercise 9

What is the complete half reaction for $3/2\ O^{o}_2 \longrightarrow 3\ O^{-2}$?

This half-reaction is an example of reduction. In this case the oxygen gains electrons and the oxidation number of O_2 is reduced. Reduction is a gain of electrons and a decrease in oxidation number. The two half-reactions may now be written and the overall equation obtained.

$2Fe^{o} - 6\ e^{-} \longrightarrow 2Fe^{+3}$ oxidation

$3/2\ O_2^{\,o} + 6\ e^{-} \longrightarrow 3\ O^{-2}$ reduction

$2Fe + 3/2\ O_2 \longrightarrow Fe_2O_3$ overall

Consider now the problem of the blast furnace (question No. 3).

Exercise 10

What is the balanced half-reaction for $2Fe^{3+} \longrightarrow 2Fe^{o}$?

Exercise 11

Is this reaction an oxidation or a reduction half-reaction?

Exercise 12

What is the balanced half-reaction for $3/2\ C^{o} \longrightarrow 3/2\ C^{4+}$?

Exercise 13

Is this reaction an oxidation or reduction half-reaction?

Exercise 14

What is the overall reaction for these two half-reactions?

We observe that there are partners involved in the reaction. Missing from our overall reaction is: $3\ O^{2-} \longrightarrow 3\ O^{2-}$. Notice that there isn't no change in oxidation number nor any addition or loss of electrons.

A new term is now intoduced which is similar to, but in many cases, different than valence. The new term is "oxidation-number".

All elements in the uncombined state have an oxidation number of zero - the same as with valence.

Beyond this, the "yard sticks" for measurement are oxygen which has an oxidation number of -2, and hydrogen which has an oxidation number of +1. In those cases where neither "O" nor "H" are part of the molecule, the structure of the compound will usually indicate what values to use. Other common oxidation states are given in the prerequisites; some examples will help to illustrate what is meant by oxidation numbers.

Always remember that chemical compounds are neutral, so that the plus and minus values of the oxidation numbers in a compound must exactly balance. For example:

The reaction in the blast furnace may be written as:

$2Fe^{+3} + 6\,e \longrightarrow 2Fe^{o}$	reduction
$3/2\ C^{o} - 6\,e \longrightarrow 3/2\ C^{+4}$	oxidation
$2Fe^{+3} + 3/2\ C^{o} \longrightarrow 2Fe^{o} + 3/2\ C^{+4}$	overall
$3\,O^{-2} \longrightarrow \quad 3\,O^{-2}$	add partners
$Fe_2O_3 + 3/2\ C \longrightarrow 2Fe + 3/2\ CO_2$	complete

Thus in each equation, something is oxidized and something else is reduced; often, a substance is just a partner and is neither oxidized nor reduced.

The important lesson to learn from the above is that:

Oxidation is the loss of electrons.

Reduction is the gain of electrons.

The gain and loss of electrons must balance between the two half-reactions.

To summarize, all elements in their natural state have - by definition - an oxidation number of zero. Therefore, in the above reaction, Fe, C, O_2 are all elements in their natural state and thus all have oxidation numbers of zero. The Periodic Table is a good guide as to the oxidation numbers that elements tend to have when combined to form compounds. The "tend" is underlined because many elements have several oxidation numbers depending upon a variety of factors; knowing what these are is an important aspect of chemistry - a prerequisite - that the student must understand.

Compound	Oxidation Number	
	+	-
O_2	0	0
H_2	0	0
H_2O	2 H's = 2x1 = 2	O = -2
N_2	0	0
NH_3	3 H's = 3x1 = 3	N = -3
SO_2	S = 4	2 O's = 2(-2) = -4
SO_3	S = 6	3 O's = 3(-2) = -6
H_2SO_4	2 H's = 2] = 8 S = 6]	4 O's = 4(-2) = -8

A close look at the above shows that O_2, H_2, N_2 are elements in their natural state, so their oxidation numbers are all zero.

H_2O has two H's and one O, so we have respectively, 2x1 = 2 and [1x(-2)] = -2. The compound is neutral.

Since NH_3 has three H's, the N must have an oxidation number of -3.

Similar reasoning applies to SO_2 and SO_3. In SO_2 the sulphur must have an oxidation number of +4, since two O's equal [2x(-2)] = -4. With SO_3, the sulphur must have an oxidation number of +6 to balance the three O's.

In the case of H_2SO_4, the two H's = +2, and the four O's = -8, thus the sulphur must have an oxidation number of +6, to balance the -8 of the four O's.

Exercise 15

Now see what you can do with the following:

Compound	Oxidation Number	
	+	-
H_2SO_3		
P_2O_5		
CO		
CO_2		
H_3PO_4		
HCl		
$HClO_3$		

In the above cases, H's and/or O's are present to indicate what values to assign the other elements. There are many chemical compounds that contain neither oxygen nor hydrogen, or are sufficiently complicated that some knowledge of chemistry is needed in order to determine the proper oxidation number. Even so, the assigning of oxidation numbers to the elements in a compound is usually obvious. For example, in the compound NaCl we know Na is in Group I-A and has an oxidation number of +1. Therefore, Cl would have an oxidation number of -1.

Exercise 16

What would be the (+) and (-) oxidation numbers for all elements in,

(a) KNO_3

(b) K_2HPO_4

(c) NH_4OH

Note that nitrogen has an oxidation number of +5 in KNO_3 and -3 in NH_4OH. This is an example of why it was said that "many elements have a variety of oxidation numbers depending upon a variety of factors."

Exercise 17

What are the oxidation numbers for the following:

Compound	Oxidation Numbers	
	+	-
$K_2Cr_2O_7$		
$CrCl_3$		
$KMnO_4$		
MnO_2		
$Mn(OH)_2$		
Na_2SO_4		
$Na_2S_2O_3$		
I_2		
HI		
HIO_3		

Now to apply oxidation numbers to the balancing of reactions involving oxidation-reduction. To do so, remember that:

(a) the positive and negative oxidation numbers assigned to the elements of a compound must balance.

(b) the positive and negative oxidation numbers assigned to the elements of a complex must equal the charge on that ion.

(c) in every reaction, something is reduced and something oxidized.

(d) oxidation means the losing of electrons.

(e) reduction means the gaining of electrons.

(f) the reactants and products of the reaction must be given.

(g) there must be the same number of electrons involved in each half-reaction.

Let's start with an easy one; note that the equation isn't balanced but that the reactants and products are given:

Given: $Zn^o + H^+ \longrightarrow Zn^{+2} + H_2^o$

$Zn^o - 2\,e \longrightarrow Zn^{+2}$ oxidation

$2H^+ + 2\,e \longrightarrow H_2^o$ reduction

$Zn^o + 2H^+ \longrightarrow Zn^{+2} + H_2^o$ overall

$2Cl^- \longrightarrow 2Cl^-$ partners

$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$ complete

Now it is your turn to balance an equation. Consider the following reaction:

$$Al^o + H^+ \longrightarrow Al^{3+} + H_2^o$$

Exercise 18

What is the balanced oxidation half-reaction?

Exercise 19

What is the balanced reduction half-reaction?

Exercise 20

What must you multiply the oxidation half-reaction and the reduction half-reaction by in order to get the same number of electrons involved in each half-reaction?

Exercise 21

What is the overall balanced equation?

A classic oxidation-reduction reaction is:

$Cu + HNO_3 \longrightarrow Cu^{+2} + NO(g) + H_2O$

$Cu - 2\,e \longrightarrow Cu^{+2}$ oxidation

$(NO_3)^{-1} \longrightarrow NO^o(g)$ reduction

The oxidation step should be obvious, but the reduction step may require some explanation. A chemical equation must balance; there must be the same number of elements on both sides of the equation. Also, we are dealing with aqueous solutions, so that H_2O, H^+, and OH^- may be added to each side of an equation in order to balance it. Thus to balance the above reduction half reaction:

$$(\overset{+5}{N}O_3)^{-1} + 4H^+ + 3\,e \longrightarrow \overset{+2}{N}O(g) + 2H_2O$$

To balance this half-reaction, it is necessary to add 2 O's (as water) to the right side of the equation, thus requiring $4H^+$ on the left. Note that the nitrate radical has a charge of -1. The 3 O's account for a charge of 3(-2) = -6, but one of these gives the nitrate radical its valence of -1; to balance the remaining -5, nitrogen must have an oxidation number of +5. As for the NO, it is a gas and the N must have an oxidation number of +2 to balance the -2 of the oxygen. Since the nitrogen goes from +5 to +2, it has to gain 3 electrons. Now we have:

$3x \quad Cu^o - 2\ e \longrightarrow Cu^{+2}$ oxidation

$2x \quad (NO_3)^{-1} + 4H^+ + 3\ e \longrightarrow NO(g) + 2H_2O$ reduction

---

$3Cu^o + 2(NO_3)^{-1} + 8H^+ \longrightarrow 3Cu^{+2} + 2NO(g) + 4H_2O$ overall

$6(NO_3)^{-1} \longrightarrow 6(NO_3)^{-1}$ partners

$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO(g) + 4H_2O$ complete

The oxidation step was multiplied by 3, and the reduction step by 2 so that each half reaction had the same number of electrons; note that the entire equations were multiplied by these amounts.

Now you try to balance a similar equation:

$$Cu^o + HNO_3 \longrightarrow Cu^{+2} + NO_2(g) + H_2O$$

The oxidation half-reaction should offer no problem at this time.

Exercise 22

What is the balanced oxidation half-reaction?

Be careful with the reduction half-reaction. Ask yourself the following:

Exercise 23

What is changing its oxidation number?

Exercise 24

Write the balanced reduction half-reaction.

Exercise 25

Now combine the two half-reactions, balance the electrons, add partners and write the complete equation.

One of the oxidation-reduction reactions used in a later study guide is:

Given: $Fe^{+2} + (Cr_2O_7)^{-2} \longrightarrow Fe^{+3} + Cr^{+3}$

$$\begin{array}{lll}
6x & Fe^{+2} - e \longrightarrow Fe^{+3} & \text{oxidation}\\
1x & (Cr_2O_7)^{-2} + 14H^+ + 6e \longrightarrow 2Cr^{+3} + 7H_2O & \text{reduction}\\ \hline
 & 6Fe^{+2} + (Cr_2O_7)^{-2} + 14H^+ \longrightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O & \text{overall}\\
 & 12(SO_4)^{-2} \longrightarrow 12(SO_4)^{-2} & \text{partners}\\ \hline
 & 6FeSO_4 + H_2Cr_2O_7 + 6H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O & \text{complete}
\end{array}$$

Balance some other oxidation-reduction reactions you will use later on:

Exercise 26

$(Cr_2O_7)^{-2} + I^{-1} \longrightarrow I_2 + Cr^{+3}$

Exercise 27

$I_2 + Na_2S_2O_3 \longrightarrow I^{-1} + Na_2S_4O_6$

Exercise 28

$$Fe^{+2} + (MnO_4)^{-1} \longrightarrow Fe^{+3} + Mn^{+2}$$

Exercise 29

$$Mn^{+2} + O_2 \longrightarrow Mn^{+4} + H_2O$$

If by now you have the swing of it, the following equations should be fairly easy for you to balance:

Exercise 30

$$(MnO_4)^{-1} + (NO_2)^{-1} + H_2O \longrightarrow MnO_2(s) + (NO_3)^{-1} + (OH)^{-1}$$

Exercise 31

$$MnO_2(s) + Cl^{-1} \longrightarrow Mn^{+2} + Cl_2$$

Exercise 32

$$H_2SO_4 + HI \longrightarrow H_2S + I_2 + H_2O$$

Exercise 33

$$Ag + (NO_3)^{-1} \longrightarrow Ag^{+1} + NO(g)$$

Exercise 34

$$Zn + HNO_3 \longrightarrow Zn^{+2} + N_2O(g) + H_2O$$

You may find that the next five equations are more difficult; if you can do these without help, you have a good comprehension of oxidation-reduction reactions:

Exercise 35

$$HCl_3 \longrightarrow HClO_4 + ClO_2(g) + H_2O$$

Exercise 36

$$H_2S + H_2O_2 \longrightarrow S + H_2O$$

Exercise 37

$$(MnO_4)^{-1} + S^{-2} + H_2O \longrightarrow MnO_2(s) + S + (OH)^{-1}$$

Exercise 38

$$ZnS + O_2 \longrightarrow ZnO + SO_2(g)$$

Exercise 39

$$C_2H_4 + (MnO_4)^{-1} \longrightarrow Mn^{+2} + CO_2(g)$$

ANSWERS

A. Pretest

1. a. Ca^{+2}, O^{-2}
   b. N^{-3}, H^{+1}
   c. N^{+4}, O^{-2}
   d. H^{+1}, S^{+6}, O^{-2}
   e. Ca^{+2}, N^{+5}, O^{-2}
   f. Fe^{+2}, I^{-1}

2.

	Element oxidized:	reduced:	oxidizing agent:	reducing agent
a.	Fe	Cl	Cl	Fe
b.	Cu	S	S	Cu
c.	S	N	N	S

3. a. $2Fe + 3Cl_2 \longrightarrow 2FeCl_3$
   b. $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
   c. $3PbS + 8HNO_3 \longrightarrow 2Pb(NO_3)_2 + 3S + 4H_2O + 2NO$

B. Study Guide

Exercise 1 - Fe_2O_3

Exercise 2 - $2Fe + 3/2\ O_2 \longrightarrow Fe_2O_3$

Exercise 3 - $Fe_2O_3 + 3/2\ C \longrightarrow 2Fe + 3/2\ CO_2$

Exercise 4 - Three.

Exercise 5

Removed. Electrons possess a negative charge. We take the value 0 and ask "How can we change to +3 by using electrons (-1)?" We have two choices 0 + (-3) or 0 - (-3). The second choice would give the correct answer (+3). The first choice would give an answer of -3.

Exercise 6 - Six electrons are added.

Exercise 7 - $2Fe^{\circ} - 6\ e^- \longrightarrow 2Fe^{3+}$

Exercise 8

Six electrons are gained. A charge of 0 must be changed to a total charge of 6-. In order to do this we must add six electrons. 0 + (-6) = -6.

Exercise 9 - $3/2\ O_2^{\circ} + 6\ e- \longrightarrow 3\ O^{2-}$

Exercise 10 - $2Fe^{3+} + 6\ e^- \longrightarrow 2Fe^{\circ}$

Exercise 11 - Reduction.

Exercise 12 - $3/2\ C^{\circ} - 6\ e^- \longrightarrow 3/2\ C^{4+}$

Exercise 13 - Oxidation.

Exercise 14 - $2Fe^{3+} + 3/2\ C^{\circ} \longrightarrow 2Fe^{\circ} + 3/2\ C^{4+}$

Exercise 15

	+	-
H_2SO_3	$\left.\begin{array}{r}2\text{ H's} = 2\\ \text{S} = +4\end{array}\right] = 6$	3 O's = -6
P_2O_5	2 P's = 10	5 O's = -10
CO	C = 2	O = -2
CO_2	C = 4	2 O's = -4
H_3PO_4	$\left.\begin{array}{r}3\text{ H's} = 3\\ \text{P} = 5\end{array}\right] = 8$	4 O's = -8
HCl	H = 1	Cl = -1
$HClO_3$	$\left.\begin{array}{r}\text{H} = 1\\ \text{Cl} = 5\end{array}\right] = 6$	3 O's = -6

Exercise 16

	Oxidation Numbers	
	+	-
(a) KNO_3	K = +1 N = +5 = +6	3 O's = 3(-2) = -6
(b) K_2HPO_4	2K = +2 H = +1 P = +5 = +8	4 O's = 4(-2) = -8
(c) NH_4OH	5 H's = +5	O = -2 N = -3 = -5

Exercise 17

Compound	Oxidation Numbers	
	+	-
$K_2Cr_2O_7$	2 K's = +2 2 Cr's = +12 = +14	7 O's = -14
$CrCl_3$	Cr = +3	3 Cl's = -3
$KMnO_4$	K = +1 Mn = +7 = +8	4 O's = -8
MnO_2	Mn = +4	2 O's = -4
$Mn(OH)_2$	Mn = +2	$2(OH)^{-1}$ = -2
Na_2SO_4	2 Na's = +2 S = +6 = +8	4 O's = -8
$Na_2S_2O_3$	2 Na's = +2 2 S's = +4 = +6	3 O's = -6
I_2	0	0
HI	H = 1	I = -1
HIO_3	H = +1 I = +5 = +6	3 O's = -6

Exercise 18 - $Al^{\circ} \longrightarrow Al^{3+} + 3\ e^-$

Exercise 19 - $2H^+ + 2\ e^- \longrightarrow H_2^{\circ}$

Exercise 20 - Oxidation - multiply by 2; Reduction - multiply by 3.

Exercise 21 - $2Al^{\circ} + 6H^+ \longrightarrow 2Al^{3+} + 3H_2^{\circ}$

Exercise 22 - $Cu^{\circ} - 2e \longrightarrow Cu^{2+}$

Exercise 23 - Nitrogen is changing its oxidation number.

Exercise 24 - $\overset{5+}{(NO_3)}^{-1} + 2H^+ + 1e \longrightarrow \overset{4+}{NO_2}(g) + H_2O$

Exercise 25

2x $Cu^o - 2e \longrightarrow Cu^{2+}$ oxidation

1x $\overset{5+}{(NO_3)}^{-1} + 2H^+ + 1e \longrightarrow \overset{4+}{4NO_2}(g) + H_2O$ reduction

$Cu^o + 2(NO_3)^{-1} + 4H^+ \longrightarrow Cu^{2+} + 2NO_2(g) + 2H_2O$ overall

$2(NO_3)^{-1} \longrightarrow 2(NO_3)^{-1}$ partners

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2(g) + 2H_2O$ complete

Exercise 26

$(Cr_2O_7)^{-2} + I^{-1} \longrightarrow I_2 + Cr^{3+}$

1x $(Cr_2O_7)^{-2} + 14H^+ + 6e \longrightarrow \overset{2x3}{2Cr} + 7H_2O$ oxidation

3x $2I^- - 2e \longrightarrow I_2$ reduction

$(Cr_2O_7)^{-2} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$ overall

$3(SO_4)^{-2} \longrightarrow 3(SO_4)^{-2}$ partners

$H_2Cr_2O_7 + 6HI + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 7H_2O + 3I_2$ complete

Exercise 27

$I_2 + Na_2S_2O_3 \longrightarrow I^- + Na_2S_4O_6$ given

$I_2 + 2e \longrightarrow 2I^{-1}$ reduction

$2(\overset{2x2}{S_2}O_3)^{-2} - 2e \longrightarrow (\overset{4x5/2}{S_4}O_6)^{-2}$ oxidation

$2(S_2O_3)^{-2} + I_2 \longrightarrow 2I^{-1} + (S_4O_6)^{-2}$ overall

$4Na^+ \longrightarrow 4Na^+$ partners

$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$ complete

Exercise 28

$Fe^{+2} + (MnO_4)^{-1} \longrightarrow Fe^{+3} + Mn^{+2}$ given

5x $Fe^{+2} - e \longrightarrow Fe^{+3}$ oxidation

1x $(MN^7O_4)^{-1} + 8H^+ + 5e \longrightarrow Mn^{+2} + 4H_2O$ reduction

$5Fe^{+2} + (MnO_4)^{-1} + 8H^+ \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$ overall

$17Cl^- \longrightarrow 17\ Cl^-$ partners

$5FeCl_2 + HMnO_4 + 7\ HCl \longrightarrow 5FeCl_3 + MnCl_2 + 4H_2O$ complete

Exercise 29

$Mn^{+2} + O_2 \longrightarrow Mn^{+4} + H_2O$ given

$Mn^{+2} - 2e \longrightarrow Mn^{+4}$ oxidation

$O_2^{\circ} + 2H^+ + 4e \longrightarrow \overset{2(\ -1)}{2(OH)}{}^{-1}$ reduction

$2Mn^{+2} + O_2 + 2H^+ \longrightarrow 2Mn^{+4} + 2(OH)^{-1}$ overall

$6(OH)^{-1} \longrightarrow 6(OH)^{-1}$ partners

$2Mn(OH)_2 + 2H_2O + O_2 \longrightarrow 2Mn(OH)_4$ complete

Exercise 30

$(MnO_4)^{-1} + (NO_2)^{-1} + H_2O \longrightarrow MnO_2(S) + (NO_3)^{-1} + (OH)^{-1}$ given

2x $\overset{7+}{(MnO_4)}{}^{-1} + 4H^+ + 3e \longrightarrow \overset{4+}{MnO_2} + 2H_2O$ reduction

3x $\overset{3+}{(NO_2)}{}^{-1} + H_2O - 2e \longrightarrow \overset{5+}{(NO_3)}{}^{-1} + 2H^+$ oxidation

$2(MnO_4)^{-1} + 8H^+ + 3(NO_2)^{-1} + 3H_2O \longrightarrow 2MnO_2 + 4H_2O +$
$3(NO_3)^{-1} + 6H^+$ overall

$2HMnO_4 + 3HNO_2 + 3H_2O + 3H^+ \longrightarrow 2MnO_2 + 4H_2O + 3HNO_3 + 3H^+$

Exercise 31

$$\begin{array}{lll}
 & MnO_2 + Cl^{-1} \longrightarrow Mn^{+2} + Cl_2 & \text{given} \\
 & \overset{4+}{Mn}O_2 + 4H^+ + 2e \longrightarrow Mn^{+2} + 2H_2O & \text{reduction} \\
 & 2Cl^{-1} - 2e \longrightarrow Cl_2 & \text{oxidation} \\ \hline
 & MnO_2 + 4HCl + 2H^+ \longrightarrow Mn^{+2} + Cl_2 + 2H_2O & \text{overall} \\
 & 2Cl^- \longrightarrow 2Cl^- & \text{partners} \\ \hline
 & MnO_2 + 6HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O & \text{complete}
\end{array}$$

Exercise 32

$$\begin{array}{lll}
 & H_2SO_4 + HI \longrightarrow H_2S + I_2 + H_2O & \text{given} \\
1x & (\overset{(6+)}{S}O_4)^{-2} + 8H^+ + 8e \longrightarrow S^{-2} + 4H_2O & \text{reduction} \\
4x & 2I^- - 2e \longrightarrow I_2 & \text{oxidation} \\ \hline
 & (SO_4)^{-2} + 8H^+ + 8I^- \longrightarrow S^{-2} + 4H_2O + 4I_2 & \text{overall} \\
 & 2H^+ \longrightarrow 2H^+ & \text{partners} \\ \hline
 & H_2SO_4 + 8HI \longrightarrow H_2S + 4H_2O + 4I_2 & \text{complete}
\end{array}$$

Exercise 33

$$\begin{array}{lll}
 & Ag + (NO_3)^{-1} \longrightarrow Ag^{+1} + NO(g) & \text{given} \\
3x & Ag^o - e \longrightarrow Ag^{+1} & \text{oxidation} \\
1x & (\overset{(5+)}{N}O_3)^{-1} + 4H^+ + 3e \longrightarrow \overset{(2+)}{N}O(g) + 2H_2O & \text{reduction} \\ \hline
 & 3Ag^o + (NO_3)^{-1} + 4H^+ \longrightarrow 3Ag^{+1} + (NO)(g) + 2H_2O & \text{overall} \\
 & 3(NO_3)^{-1} \longrightarrow 3(NO_3)^{-1} & \text{partners} \\ \hline
 & 3Ag^o + 4HNO_3 \longrightarrow 3Ag(NO_3) + NO(g) + 2H_2O & \text{complete}
\end{array}$$

Exercise 34

$2Zn + HNO_3 \longrightarrow Zn^{+2} + N_2O(g) + H_2O$ given

4x $Zn^{o} - 2e \longrightarrow Zn^{+2}$ oxidation

1x $2(\overset{5+}{NO_3})^{-1} + 10H^{+} + 8e \longrightarrow \overset{2+}{N_2O}(g) + 5H_2O$ reduction

$4Zn + 2(NO_3)^{-1} + 10H^{+} \longrightarrow 4Zn^{+2} + N_2O(g) + 5H_2O$ overall

$8(NO_3)^{-1} \longrightarrow 8(NO_3)^{-1}$ partners

$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O(g) + 5H_2O$ complete

Exercise 35

In this reaction, the $HClO_3$ is both oxidized and reduced:

$HClO_3 \longrightarrow HClO_4 + ClO_2(g) + H_2O$ given

1x $(\overset{5+}{ClO_3})^{-1} + H_2O - 2e \longrightarrow (\overset{+7}{ClO_4})^{-1} + 4H^{+}$ oxidation

2x $(\overset{5+}{ClO_3})^{-1} + 2H^{+} + 2 \longrightarrow \overset{4+}{ClO_2}(g) + H_2O$ reduction

$2(ClO_3)^{-1} + 4H^{+} + H_2O \longrightarrow 2(ClO_4)^{-1} + 4H^{+} +$
$2ClO_2 + 2H_2O$ overall

$2HClO_3 \longrightarrow 2HClO_4 + 2ClO_2 + H_2O$ complete

Exercise 36

In the case of peroxide, oxygen has an oxidation number of -1.

$H_2S + H_2O_2 \longrightarrow S + H_2O$ given

$S^{-2} - 2e \longrightarrow S^{o}$ oxidation

$2\,O^{-1} + 4H^{+} + 2e \longrightarrow 2H_2O$ reduction

$S^{-2} + 2\,O^{1-} + 4H^{+} \longrightarrow S^{o} + 2H_2O$ overall

$H_2S + H_2O_2 \longrightarrow S^{o} + 2H_2O$ complete

Exercise 37

This reaction calls for a basic solution.

$(MnO_4)^{-1} + S^{-2} + H_2O \longrightarrow MnO_2 + S + (OH)^{-1}$ given

2x $\overset{7+}{(MnO_4)}^{-1} + 4H^+ + 3e \longrightarrow \overset{4+}{MnO_2} + 2H_2O$ reduction

3x $S^{-2} - 2e \longrightarrow S^\circ$ oxidation

$2(MnO_4)^{-1} + 8K^+ + 3S^{-2} \longrightarrow 2MnO_2 + 4H_2O + 3S^\circ$ overall

$2K^+ + 2(OH)^{-1} \longrightarrow 2K^+ + 2(OH)^{-1}$ partners

$2KMnO_4 + 3H_2S + 2H_2O \longrightarrow 2MnO_2 + 4H_2O + 3S + 2KOH$

$2KMnO_4 + 3H_2S \longrightarrow 2MnO_2 + 2H_2O + 3S + 2KOH$ complete

Exercise 38

Note in the following that the Zn^{+2} does not change valence.

$ZnS + O_2 \longrightarrow ZnO + SO_2(g)$ given

2x $S^{-2} + 2H_2O - 6e \longrightarrow \overset{4+}{SO_2} + 4H^+$ oxidation

3x $O_2^\circ + 4e \longrightarrow 2\,O^{2-}$ reduction

$2S^{-2} + 4H_2O + 3\,O_2 \longrightarrow 2SO_2 + 8H^+ + 6\,O^{-2}$ overall

$2Zn^{+2} \longrightarrow 2Zn^{+2}$ partners

$2ZnS + 4H_2O + 3\,O_2 \longrightarrow 2ZnO + 4H_2O + 2SO_2$

$2ZnS + 3\,O_2 \longrightarrow 2ZnO + 2SO_2$ complete

Exercise 39

This is an example where an organic compound is involved.

$C_2H_4 + (MnO_4)^{-1} \longrightarrow Mn^{+2} + CO_2(g)$ given

5x $\overset{2(2-)}{C_2H_4} + 2H_2O - 8e \longrightarrow \overset{+4}{CO_2} + 8H^+$ oxidation

8x $\overset{7+}{(MnO_4)}^{-1} + 8H^+ + 5e \longrightarrow Mn^{+2} + 4H_2O$ reduction

$5C_2H_4 + 10H_2O + 8(MnO_4)^{-1} + 64H^+ \longrightarrow 5CO_2 + 40H^+ + 8Mn^{+2} + 32H_2O$ overall

$16Cl^- \longrightarrow 16Cl^-$ partners

$5C_2H_4 + 8MnO_4 + 16\,HCl \longrightarrow 5CO_2 + 8MnCl_2 + 22H_2O$ complete

ELECTROCHEMISTRY

SUMMARY

Water is perhaps the closest thing there is to a universal solvent. In general, the chemist recognizes two broad classes of compounds: those aqueous solutions that conduct electricity and those which do not. This mini-course looks into the behavior of those chemicals which, in aqueous solutions, do conduct electricity. These are known as electrolytes, and the quantitative measurement of conductivity is covered in this mini-course.

If an electric current - usually D.C. - is passed through an aqueous solution of an electrolyte, something usually happens. Metals are deposited or eaten away; gases are produced. These phenomena are developed and explained. Also, two different substances - two different metals for instance - often generate an electric current, and usually with some destructive effects. This side of electrochemistry is also developed.

RATIONALE

The study of electrochemistry could be a year's course. It is particularly important to the water chemist since so many of the reactions he encounters in the laboratory involve electrolytes; their behavior may be the basis of their analytical determination. Thus one of the main objectives of this mini-course would be to pursue the study of electrochemistry beyond what could be covered here. Hopefully, the foundation for such self study has been provided.

ACKNOWLEDGEMENT

The author is indebted to Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College, for his help and advice in posing and answering many of the questions that follow.

PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. Differentiate between strong electrolytes, weak electrolytes, and nonelectrolytes.
2. Use equilibrium constants to calculate the concentrations of ions in solution of an insoluble salt.
3. Convert from moles/l to g/l and to ppm.
4. Use Ohm's law.

OBJECTIVES

After completing this mini-course, the student should be able to:

1. Diagram a conductivity cell and a Wheatstone Bridge and discuss the function of each portion of the apparatus. The discussion should include the nature of the solution and electrodes in the conductivity cell.

2. Discuss the method for determining resistance, conductance, specific conductance, equivalent conductance at infinite dilution.

3. Given conductance data at various concentrations, determine the specific conductance and equivalent conductance at infinite dilution.

4. Interconvert between resistance and conductance.

5. Define free energy, enthalpy, and entropy.

6. Given the solubility of an electrolyte in water, discuss the relationship between the free energy, enthalpy, and entropy. Include the statement that when a system is in equilibrium the free energy is zero.

7. Use a table of oxidation (or reduction) potentials to determine whether a given reaction is spontaneous.

8. Discuss electrolysis with respect to strong and weak electrolytes, including anodic and cathodic equations.

9. Explain why H_2 and Cl_2 and NaOH are the products of the electrolysis of aqueous NaCl, and Cu, O_2, and H_2SO_4 are the products of the electrolysis of aqueous $CuSO_4$.

10. Use a table of oxidation (or reduction) potentials to predict the products of the electrolysis of a given compound.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. The salt, AgCl, has a value of $K = 1.1 \times 10^{-10}$. What would you predict would happen when solid AgCl is added to water?

a. Free energy: (1) ⊕, (2) ⊖, (3) zero, (4) can't tell.

b. Enthalpy: (1) exothermic, (2) endothermic, (3) negligible.

c. Entropy: (1) increases, (2) decreases, (3) no change, (4) can't tell.

2. Identify each of the following as (1) strong, (2) weak, or (3)non-electrolytes.

a. NaCl
b. sugar
c. H_2SO_4
d. CH_3COOH
e. NaOH
f. NH_4OH

3. An increase in the degree of randomness of a system shows an increase in: (1) enthalpy, (2) free energy, (3) entropy, (4) conductance, (5) oxidation potential.

4. Diagram a Wheatstone Bridge and label the various portions.

5. Diagram a conductivity cell and relate it to the diagram in #4, above.

6. Replot the data for NaAc on page 15 and redetermine the equivalent conductance at infinite dilution.

7. Discuss the electrolysis of $CuSO_4$, including equations.

8. Would the reaction: $Fe + Mg^{+2} \longrightarrow Fe^{+2} + Mg$, be spontaneous? Why or why not?

I. INTRODUCTION

A. Electrolytes

Chemically, physically, biologically - any way you look at it - water is one of the most unusual and essential substances on the face of the earth.

Exercise 1

What are three reasons why you think water is an unusual and essential substance?

Water ionizes and forms H^+ and OH^-. You have studied this in a previous mini-course.

Exercise 2

What is the equation for the ionization of water?

Exercise 3

What is the equilibrium expression and value for K_w?

Exercise 4

What are the $[H^+]$ and $[OH^-]$ concentrations in pure water?

The answers to the previous exercises should tell you several important things about water.

Exercise 5

How many g/1 and ppm of $[H^+]$ and $[OH^-]$ are in water.

Exercise 6

Would you expect water to be acidic, neutral or basic and why?

Exercise 7

Would you expect water to conduct electricity and if so why?

Many aqueous solutions conduct electricity very readily. If a substance is soluble in water and the solution conducts electricity, that substance is known as an electrolyte.

Exercise 8

Give the formula for several common strong electrolytes.

Exercise 9

What are several weak electrolytes?

Exercise 10

What are several non-electrolytes?

At this point, the thoughtful student should ask: why does an electrolyte conduct electricity? The classic answer is rather simple - because ions are formed. But classic answers often leave much unanswered:

(a) We know that a crystal of NaCl is made of Na^+ and Cl^-, and that powerful forces hold the oppositely charges particles together. What greater forces pull the crystal apart when it dissolves in water?

(b) H_2SO_4 is made in huge amounts; its production is sometimes used as a measure of civilization - the more H_2SO_4 produced by a country, the more civilized it is. (Certainly this gives the thoughtful student much to ponder.) One hundred percent H_2SO_4 is transported in steel tanks because it is not ionized; otherwise it would dissolve the tanks and/or blow them to bits due to the formation of H_2 gas. Why are H^+ and SO_4^{--} formed when H_2SO_4 is dissolved in water?

(c) $BaSO_4$ is an ionic crystal. It is not soluble in water to any appreciable extent. Why, when placed in water, are the forces holding this crystal together stronger than the forces holding NaCl together?

B. Free Energy, Enthalpy and Entropy

Many introductory courses in chemistry introduce these concepts, but a brief review is probably in order:

Free Energy is a quantitative measure of the driving force that causes a chemical reaction to proceed spontaneously. Like water running downhill, a reaction occurs spontaneously if the change in free energy is negative, for this means that energy has flowed from a high to a lower energy level.

Enthalpy is a measure of heat transfer at constant pressure - usually atmospheric pressure.

Entropy is a concept that can be very complex, but for present purposes it is quite enough to say that entropy is a measure of chaos, randomness, disorder. The second law of thermodynamics states that the entropy of the world always increases; orderliness gives way to disorder, regularity to randomness.

The above are tied together in the highly important thermodynamic equation:

Equation (1)

Free energy = enthalpy - (Entropy x absolute temperature)

$$\Delta G = \Delta H - T\Delta S$$

Now let us apply these concepts to the forces that tear the NaCl crystal apart when it dissolves in water. Just what does happen when:

$$Na^{+}Cl^{-}(s) \xrightarrow{H_2O} Na^{+}(aq) + Cl^{-}(aq)$$

We know this reaction occurs spontaneously at room temperature, or 25°C.

Exercise 11

Is the free energy (+) or (-)?

Exercise 12

What has happened to the ordered crystalline structure?

Exercise 13

What has happened to the entropy?

We also know there is little or no heat change when NaCl is dissolved in water.

Exercise 14

What would you say about the enthalpy change?

Exercise 15

If you substitute these observations in Equation (1), what would you say about the spontaneity of the reaction?

In the case of H_2SO_4, there would be little change in entropy since H_2SO_4 is a liquid and the molecules are therefore not arranged in an orderly crystalline pattern. Furthermore, there can be no ions in concentrated H_2SO_4, otherwise it would dissolve a steel tank. However, the heat of solution in water is very large as anyone knows who has added concentrated H_2SO_4 to H_2O. Thus:

$$H_2SO_4 \xrightarrow{H_2O} 2H^{+} + SO_4^{--} \text{ minus much energy.}$$

Free energy = (large negative enthalpy) - (small entropyxtemp)

Free energy = a negative quantity, a spontaneous reaction

For relatively insoluble substances like $BaSO_4$, there is some slight solubility:

$$Ba^{++}SO_4^{--}(s) \longrightarrow Ba^{++}(aq) + SO_4^{--}(aq)$$

$$K_{sp} = [Ba^{++}][SO_4^{--}] = 1.5x10^{-9}$$

Exercise 16

What is the solubility of $BaSO_4$ in g/1?

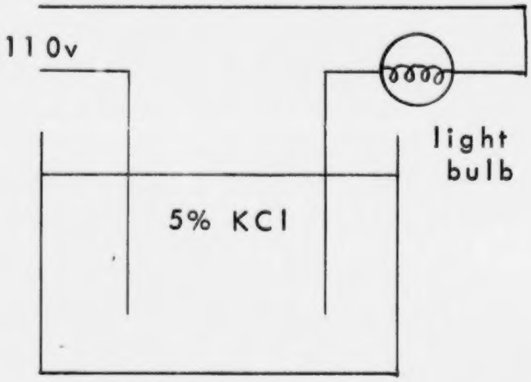
When a chemical reaction is in equilibrium, as it is in the above case, then the free energy is zero, for there is no tendency for the net reaction to proceed in either direction. The net effect is that the enthalpy equals the entropy and no concentration changes occur.

Said differently, the forces holding the $BaSO_4$ crystal together are stronger than those tending to tear it apart, since the solubility is quite low.

The above explanation of solubility phenomena in water is thermodynamically correct, but it doesn't present a clear or satisfying physical picture of what happens in that mysterious world of small particles and powerful forces. Of late, some progress has been made in these respects; even so, it's difficult to think like a molecule.

We must conclude, however, that water is a powerful agent for pulling things apart; and when those "things" are ions - or become ions - we are introduced to the study called Electrochemistry.

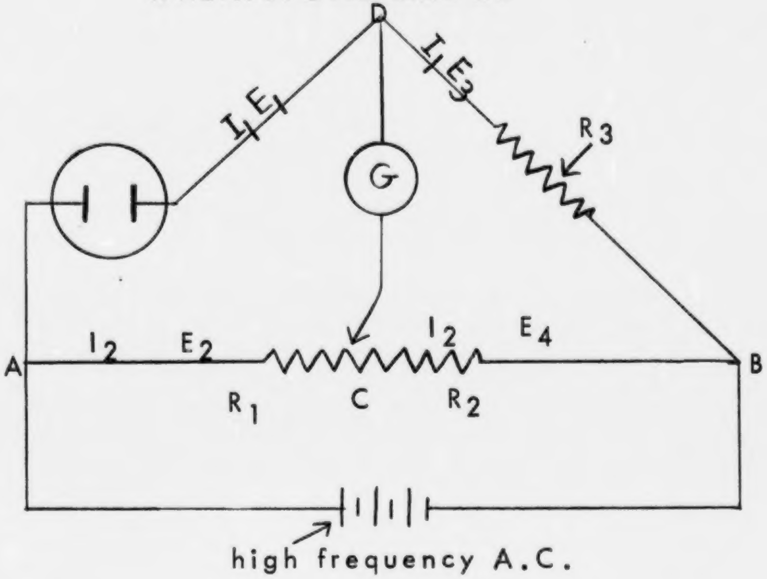
Aqueous solutions of strong electrolytes are excellent conductors or electricity. A 5% solution of KCl conducts electricity so well that in the following set-up - the bulb burns brightly:

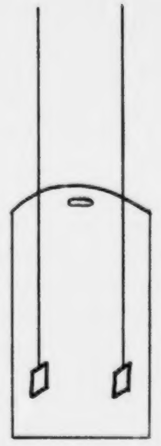


Qualitatively, the light burns; now let's see how the chemist quantitatively measures the conductivity of aqueous solutions. To do this, the solution being tested is placed in what is called a conductivity cell which is, essentially, a glass tube into which are sealed two platinum electrodes (coated with platinum black) of fixed size and distance apart. An air hole near the top of the cell allows the aqueous solution to completely cover the electrodes.

The conductivity cell is then connected to a conductivity meter, which completes the circuit of what is known as a Wheatstone Bridge. Schematically, the apparatus is four resistances hooked to a galvanometer in such a way that an unknown resistance - that of the conductivity cell - can be measured as follows:

WHEATSTONE BRIDGE





CONDUCTIVITY
CELL

Let I_1 = the current flowing thru circuit ADB

Let I_2 = " " " " " ACB

Adjustments are made so that the galvanometer reads zero; that means the potential at D = the potential at C.

That is, $E_1 = E_2$

For circuits AD, $E_1 = XI_1$ and for AC, $E_2 = R_1I_2$.

Thus $X/R_1 = I_2/I_1$

Again, because the galvanometer reads zero, the potential at D = the potential at C, and $E_3 = E_4$.

Exercise 17

For circuit DB, E_3 = what?

Exercise 18

For circuit CB, E_4 = what?

Exercise 19

R_3R_2 = what?

Exercise 20

Show how $X = \frac{R_1}{R_2} \times R_3$

In operating the conductivity meter, the ratio of R_1/R_2 is given on a dial marked "multiply by'; it reads in increments of 10. This knob is turned until a null point can be obtained by turning another knob which regulates R_3.

Conductance

Thus it is that the Wheatstone Bridge measures the resistance of the solution in the conductivity cell. The chemist apparently prefers to speak of conductance rather than resistance, so he defines conductance (L) as the reciprocal of resistance (R).

$$L = \frac{1}{R}\text{, expressed as ohms}^{-1}$$

So far, it would seem, such a determination is not quantitative; conductance is a broad term. The question could and should be asked: conductance of what?

Specific conductance

Thus it is that a conductance cell is made according to specified dimensions, which leads to the concept of specific conductance. The assumption is made - which certainly is valid - that the current in the conductivity cell is carried by the solution between the electrodes, and therefore the conductivity of the cell is directly proportional to the area of the electrode and inversely proportional to the distance between the electrodes:

$$L = k\ \frac{A}{\ell}$$

L is the conductance in ohms^{-1}

A is the cross sectional area of the cell in cm^2

ℓ is the distance between the electrodes in cm

k is the proportionality factor; it is called the specific conductance.

Specific conductance then equals the conductance when the volume between the electrodes equals 1 cm^3, for then -

$$A = 1\ cm^2 \text{ and } \ell = 1\ cm$$

$$L = k\frac{A}{\ell} = k\frac{1^2}{1}\ ,\ L = k$$

Equivalent conductance

Equivalent conductance completes our quest for a quantitative measurement, for now the concentration of the solution being tested is also stipulated. Equivalent conductance is defined as:

> "the conductivity of a solution that contains one equivalent weight of a solute when measured between electrodes that are 1 cm apart and large enough to contain the entire solution."

For example, a solution containing one equivalent weight of KCl might be one mole per liter of KCl. Therefore, a conductivity cell - imaginary, of course - would have to be made that had Pt electrodes which were 1 cm apart and 1000 cm^2 in area, so that the volume of the solution between the electrodes would equal

$$1\ cm \times 1000\ cm^2 = 1000\ cm^3 = 1 \text{ liter}$$

A solution containing one equivalent weight of KCl might also be a 0.1 mole of KCl in 10 liters of water. A conductivity cell capable of holding this much solution would have to have Pt electrodes with an area of 10,000 cm^2, 1 cm apart.

Obviously, such measurements cannot be made experimentally; they are calculated. It was stated above that;

$$\text{Conductance} = \text{specific conductance}$$

for a cell with Pt electrodes 1 cm^2 and 1 cm apart. Such a cell would contain 1 ml between electrodes. Equivalent conductance, by the above definition, would have to be 1,000 times larger for a solution containing one equivalent of a solute, 10,000 times larger for a solution containing 0.1 equivalents of solute, etc. These conditions are satisfied by the equation;

$$\Lambda = k\frac{1{,}000}{c}\ ,\ \text{where}$$

Λ is the equivalent conductance

k is the specific conductance

c is the equivalent concentration

Experimentally, it would be next to impossible to measure accurately the area of a pair of Pt electrodes and the average distance between them - particularly since the electrodes are usually sealed within a glass tube. All this is avoided in that it has been done for us. Referring to the formula

$$L = k \times \frac{A}{\ell} \qquad \text{or} \qquad k = \frac{\ell}{A} \times L$$

ℓ/A is fixed for any paricular cell in that the area of and distance between the electrodes cannot be changed; therefore, ℓ/A is called the cell constant. Using KCl as the standard (for a reason that will be explained later) the specific conductance of a 0.1 molar solution of KCl has been carefully and repeatedly measured by many investigators, resulting in an accepted value of 0.12886 ohms^{-1} at 25° C. This value is quite temperature dependent.

So what the chemist does is to immerse his conductance cell in a 0.1 molar solution of KCl at 25° C and determine the conductance (L). Suppose the resistance turns out to be 0.833 ohms.

Exercise 21

What is the value of L?

Exercise 22

What is the cell constant?

Knowing this, the conductance of any solution is determined and the specific conductance calculated.

Exercise 23

Suppose the resistance of a solution were 1.267 ohms, what is the specific conductance using the above cell constant?

If now the specific conductance of KCl is measured at several molar concentrations, the equivalent conductance can be calculated:

c Equiv./liter	k ohms^{-1}	$\triangle$
1.0	0.1119	111.9
0.1	0.012896	128.96
0.01	0.0014127	141.27
0.001	0.00014695	146.95
0.000		149.86

The zero value is obtained by extrapolation of a graph plotting C vs $\triangle$.

Since, by definition, equivalent conductance measures the conductivity of the same number of equivalent ions at various concentrations, the above data shows that the ions are more conductive as the concentration of the solution is reduced. This is explained, quite simply, by pointing out that the ions conducting the electricity are less inhibited by the attractions and repulsions of the neighboring ions - both plus and minus.

Exercise 24

What effect will making the sample more dilute have upon these ions?

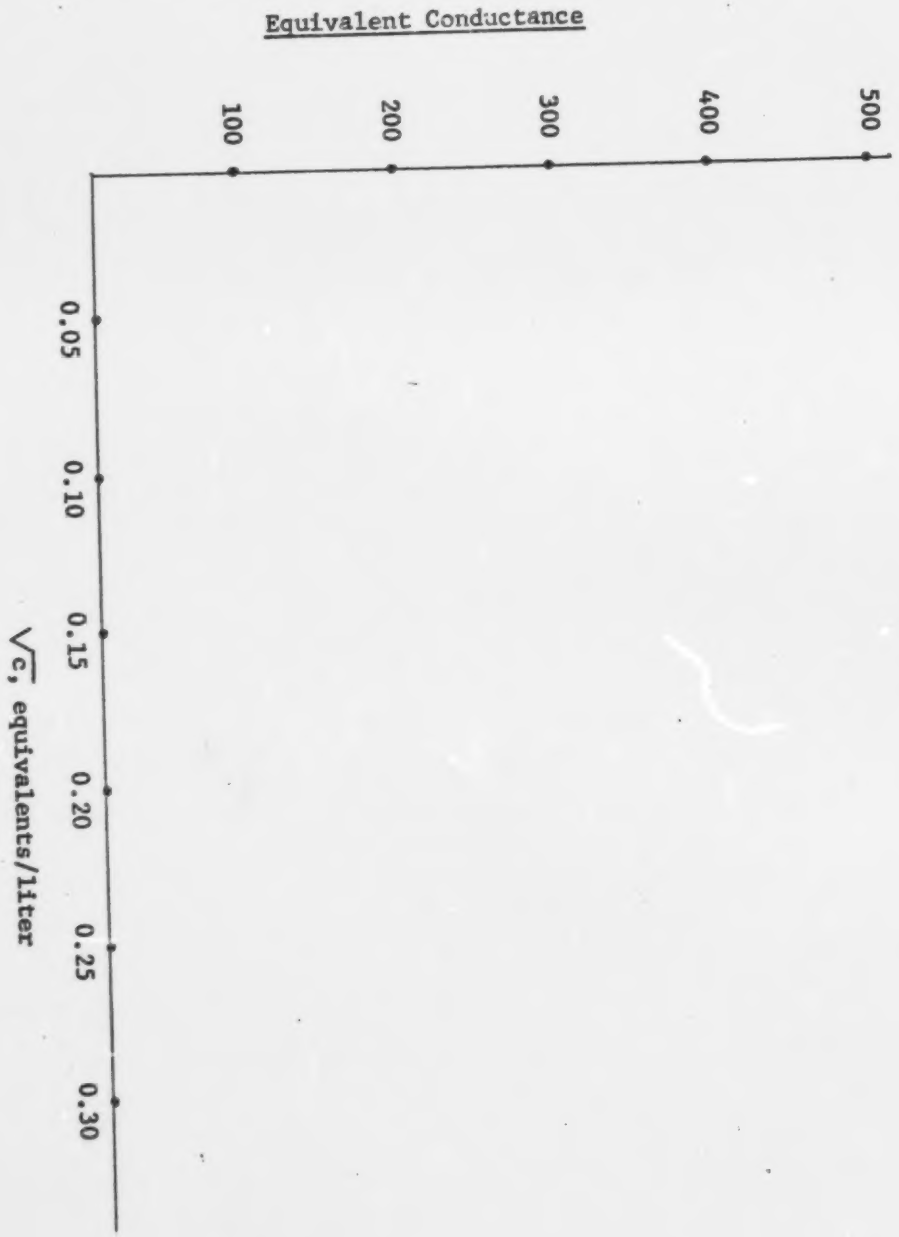
The equivalent conductance of many electrolytes has been measured and it is found that a straight line results if these values are plotted against the square root of equivalent concentration - in the case of strong electrolytes; this is not true of weak electrolytes as the following data and plots show.

Equivalents/liter

$\sqrt{c}$	c	NaCl	KCl	NaAc	H_2SO_4	HAc	NH_4OH
0	0	126.4	149.9	91.0	429.6	(390.7)	(271.4)
0.032	0.001	123.7	146.9	88.5	399.5	49.2	34
0.100	0.010	118.5	141.3	83.8	336.4	16.3	11.3
0.320	0.100	106	129.0	72.8	250.8		3.6
1.000	1.000		111.9	49.1			

Exercise 25

Plot the above data.



Exercise 26

Which line represents the strongest electrolyte?

Exercise 27

What relationship does the plotted curves tell us between conductance and the strength of an electrolyte?

Exercise 28

What relationship is evident at infinite dilution? (Infinite dilution is the extrapolated value at concentration = 0.00.)

The difference between strong and weak electrolytes is due to their degree of dissociation. Aqueous solutions of HCl, NaOH, H_2SO_4, KCl, etc., are completely ionized:

$$HCl \longrightarrow \underset{100\%}{\underline{H^+ + Cl^-}} \qquad NaOH \longrightarrow \underset{100\%}{\underline{Na^+ + OH^-}}$$

Weak solutions are partially ionized:

$$\underset{99\%}{\underline{CH_3COOH}} \longrightarrow \underset{1\%}{\underline{CH_3COO^- + H^+}}$$

$$\underset{99\%}{\underline{NH_4OH}} \longrightarrow \underset{1\%}{\underline{NH_4^+ + OH^-}}$$

Exercise 29

Since it is the ions that conduct the electricity, how would you classify acetic acid, hydrochloric acid, ammounium hydroxide and sodium hydroxide - as weak or strong acids or bases?

It should be emphasized, however, that the OH^- from the NH_4OH are exactly the same as the OH^- from the NaOH; in the latter case there are more of them. The same relationship holds for the H^+ from CH_3COOH and HCl.

By means of transference numbers - which will not be covered for lack of space, but which are not beyond the ability of an interested student to "dig" on his own - it can be shown that various ions vary considerably in their ability to carry an electric current. The equivalent conductance of a few anions and cations are given in the following table:

Equivalent conductance at infinite dilution

	Λ		Λ
H^+	349.82	OH^-	198.0
Na^+	50.11	Cl^-	75.2
K^+	73.52	CH_3COO^-	40.9
NH_4^+	73.4	SO_4^{--}	79.8
$1/2Ca^{++}$	59.5	HCO_3^-	44.5
$1/2Mg^{++}$	53.1	NO_3^-	71.4

Some pages back it was stated that KCl is used as the standard for specific conductance experiments. The above table explains why: K^+ and Cl^- have about the same equivalent conductance so that each ion conducts about half the current; this tends to stabilize electrometric determinations.

Exercise 30

According to the above table, which ions are the best conductors of electricity?

The specific conductance of the purest water is:

$$0.58x10^{-7} \text{ ohms}^{-1} \text{ at } 25^{\circ} \text{ C.}$$

Exercise 31

What is the molarity (c) of water?

Exercise 32

What is the equivalent conductance of water?

Exercise 33

Using the equivalent conductances for H^+ and OH^-, previously given, what is the total equivalent conductance of water?

Actually the equivalent conductance is only $1.05x10^{-6}$.

Exercise 34

What is the degree of ionization (or the fraction of the water that is ionized) to give an equivalent conductance of $1.05x10^{-6}$?

Exercise 35

What is the actual molar concentration (c) of H^+ and OH^-, using the data in Exercise 33 and 34?

Exercise 36

Based on your answer to Exercise 35, calculate K_w.

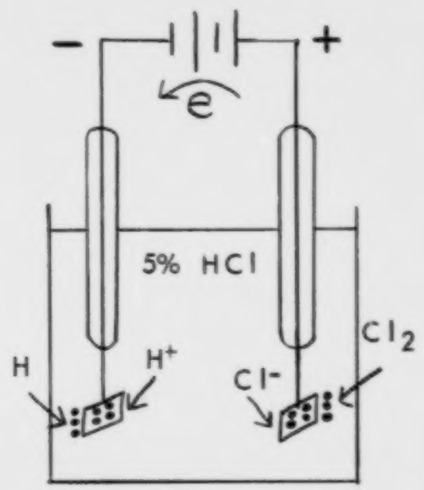
Conductivity measurements are frequently used to measure quickly the total concentrations of dissolved salts in water. The equivalent conductivities of the cations and anions might average 65 and 75 respectively, for a total of 140.

Exercise 37

Suppose the specific conductance of a water sample was measured as 125×10^{-6} $ohms^{-1}$. What is the approximate concentration of the dissolved salts in mg/l?

Electrolysis

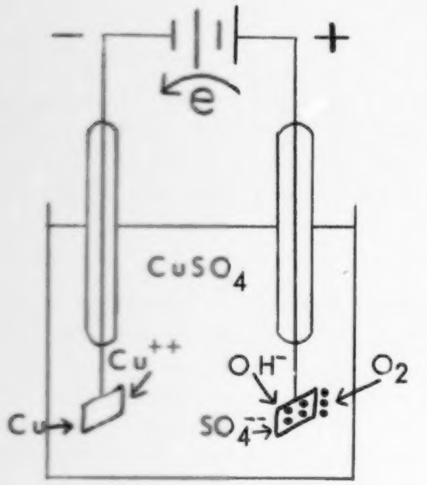
All of electrochemistry cannot be covered in one mini-course, but two more topics must be discussed because they are so important to the water chemist. The first of these is electrolysis.



If an external battery is connected to two Pt electrodes which are placed in a beaker containing 5% HCl in water, the H^+ (hydrogen ions) are attracted to the cathode where they gain electrons; H_2 (g) is liberated. The Cl^- (chloride ions) migrate to the anode and lose electrons; Cl_2 (g) is liberated. The charge carrying ions are converted to neutral molecules and released at each electrode.

The reaction which occurs at each electrode is called a half reaction. At the cathode, electrons are gained by the cations; so this is a reduction half reaction. Since electrons are lost at the anode, this is an oxidation half reaction.

If $CuSO_4$ is placed in the beaker, Cu^{++} goes to the cathode and Cu^o is deposited on the electrode. But O_2 (g) is liberated at the anode and not SO_4^{--}.



This is explained as follows: H^+ and OH^- are always present in water, and they are attracted to the negative and positive electrodes respectively. However, Cu^{++} ions are preferentially reduced to Cu^o at the cathode, rather than H^+ to H_2 (g). In other words, Cu^{++} is more easily reduced than H^+. At the anode, OH^- have a greater "escaping tendency" than SO_4^{--}, so O_2 (g) is liberated. This means OH^- is more easily oxidized than SO_4^{-}. At the anode this half reaction occurs:

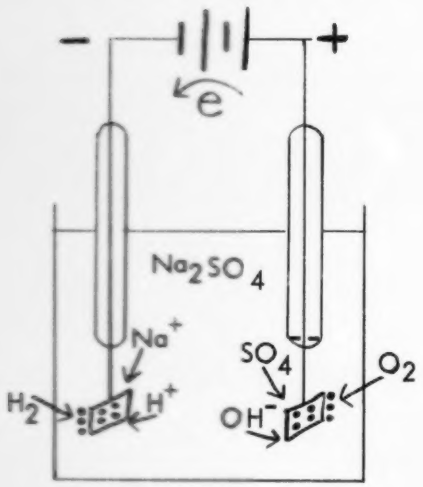
$$4(OH^-) - 4e \longrightarrow O_2\ (g) + 2H_2O$$

The $4(OH^-)$ were formerly associated with $4H^+$, so these are available to combine with the SO_4^{--} with the result that H_2SO_4 forms at the anode:

$$4H^+ + 2SO_4^{--} \longrightarrow H_2SO_4$$

Exercise 38

In this case, the charge carrying ions are discharged at which electrode?



Now let's put a solution of Na_2SO_4 in the beaker and turn on the current. As would be expected, O_2 (g) is generated at the anode, as in the above case. But at the cathode, H_2 (g) is formed. Applying the same argument as before, both H^+ and Na^+ are attracted to the cathode but H^+ is more easily reduced than Na^+. The half reaction at the anode is:

$$4H^+ + 4e \longrightarrow 2H_2$$

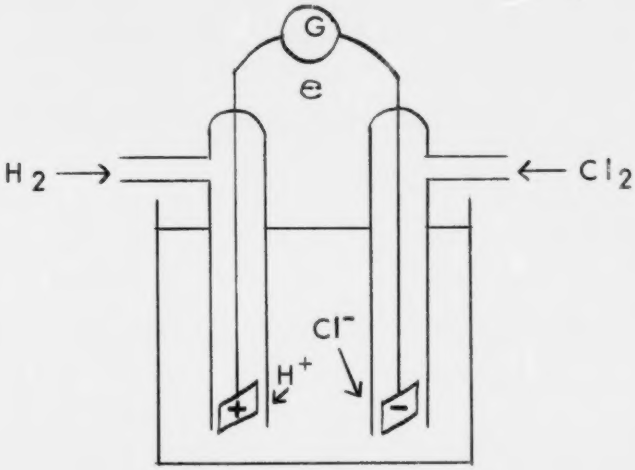
The $4H^+$ were associated with $4(OH^-)$ so these combine with the Na^+ to produce NaOH, which remains in solution as the ions.

Batteries

In the electrolysis of an aqueous solution of HCl, a battery pumps electrons through an external circuit with the net result that H_2 (g) is evolved at the cathode and Cl_2 (g) at the anode. Under these conditions, the following reaction proceeds from left to right:

$$2HCl \rightleftharpoons H_2 + Cl_2$$

This reaction - written with reverse arrows - implies that under other conditions, the reaction proceeds from right to left and thereby converts H_2 (g) and Cl_2 (g) into HCl. Then, it will be found, current actually does flow in the opposite direction and HCl is produced:



$$H_2 + Cl_2 \longrightarrow 2HCl$$

This reaction proceeds spontaneously and a galvanometer in the circuit reads 1.3595 volts.

There are numerous oxidation-reduction reactions that occur in aqueous solutions and often these spell trouble for the water chemist. Stray electrical currents act like external batteries and cause electrolysis which tends to corrode and dissolve metals and other materials of construction. Or, a combination of metals may act as a battery and be self destructive.

The chemist has devised what he calls an electrochemical series which enables him to calculate which oxidation-reduction reactions will or will not occur spontaneously. The most active reducing agents are at the top of the list and the voltage given is a measure of their relative electrochemical activity. The strongest oxidizing agents are at the bottom of the following table. The voltage of

$$1/2H_2 \longrightarrow H^+ + 1e^-$$

is arbitrarily taken as zero.

A few selected values follow: many more are given in any chemical handbook.

Half reaction	Volts at 25° C.
$K \longrightarrow K^{+} + e$	2.925
$Ca \longrightarrow Ca^{++} + 2e$	2.866
$Na \longrightarrow Na^{+} + e$	2.7142
$Mg \longrightarrow Mg^{++} + 2e$	2.363
$Al \longrightarrow Al^{+++} + 3e$	1.662
$Zn \longrightarrow Zn^{++} + 2e$	0.7628
$Fe \longrightarrow Fe^{++} + 2e$	0.4402
$H_2 \longrightarrow H^{+} + 2e$	0.0000
$Cu \longrightarrow Cu^{++} + 2e$	-0.337
$Fe^{++} \longrightarrow Fe^{+++} + e$	-0.771
$2Cl^{-} \longrightarrow Cl_2 + 2e$	-1.3595

To determine whether or not a reaction proceeds spontaneously, the above values for half reactions are combined to give the desired reaction.

The rules for this addition are to subtract the reduction equation - which is the opposite of the step shown in the table on page - from the oxidation equation. This is shown in the half-reactions below by multiplying by +1 for the oxidation step and -1 for the reduction step. If the resulting voltage is positive, then the reaction proceeds spontaneously; if negative, it goes in the opposite direction. Here are some examples:

Reaction wanted: $Cu + Cl_2 \longrightarrow CuCl_2$

Half reactions	Voltage	Multiply by
$Cu \longrightarrow Cu^{++} + 2e^{-}$	-0.337	+1
$2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$	-1.3595	-1

Add: $Cu + Cl_2 \longrightarrow Cu^{++} + 2Cl^{-}$ +1.022 volts

This reaction proceeds spontaneously as written since the voltage is positive.

Consider the following reaction:

$$2Fe^{+++} + Cu \longrightarrow Cu^{++} + 2\ Fe^{++}$$

Exercise 39

What is the half reaction and potential for the oxidation of Fe^{++}?

Exercise 40

What is the half reaction and the potential for the oxidation of Cu?

Exercise 41

What is the overall reaction and potential?

Exercise 42

Is the reaction spontaneous?

Given the following reaction $2Fe^{++} + Cl_2 \longrightarrow 2Fe^{+++} + 2Cl^-$

Exercise 43

What is the overall reaction and potential and is the reaction spontaneous?

The "multiply column" corrects for the fact that there is always oxidation at one electrode and reduction at the other. In the above table, all the half reactions are written as oxidations, so a (+) in the "multiply by" column means these values are not changed; thus a (-) actually means that this is a reduction half reaction.

This by no means completes a study of electrochemistry, but it does give the chemist some of the theory and chemical equations he will probable need. Hopefully, this mini-course will also provide sufficient foundation for further self study of electrochemistry if and when needed.

ANSWERS

A. Pretest

1. a. (1) or (3), since AgCl is essentially insoluble.
   b. (3)
   c. (1)
2. strong: a,c,e
   weak: d,f
   non-electrolytes: b
3. (3)
4. See page 203.
5. See page 203.
6. Compare to your answer to Exercise 25 and 28, and from the table on page
7. See page 212. Anode: $4\ OH^- \rightarrow O_2(g) + H_2O + 4e^-$
   Cathode: $Cu^{+2} + 2e^- \rightarrow Cu$
8. No. The potential would be -1.923, the negative value means the reaction is not spontaneous.

B. Study Guide

Exercise 1

(a) It is a liquid, yet based on its molecular weight it should be a gas. H_2S is a gas, its molecular weight is almost twice that of H_2O, and "O" and "S" are close relatives in the periodic Table.

(b) Solid water is less dense than liquid water, so ice floats. This is a most fortnate and unusual property of water, for the solid phase of almost all chemical compounds is more dense than the liquid phase. What would happen if ice were more dense than water?

(c) Water comes close to being the universal solvent. One of the main divisions of chemistry is between those substances which are soluble in water and those which are not. Even the so-called insoluble chemical compounds are more or less soluble in water as measured by their solubility product constant.

(d) Water ionizes to form H^+ and OH^- as has been emphasized in a previous mini-course.

Exercise 2

$$H_2O \longrightarrow H^+ + OH^-$$

Exercise 3

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

Exercise 4

$$[H^+] = [OH^-] = 1 \times 10^{-7}$$

Exercise 5

There are both H^+ and OH^- in water in equal amounts. That is, there are 10^{-7} moles/liter of H^+ and OH^- in water.

How many g/1 and ppm does this amount to?
Your answer should be 0.001 ppm of H^+ and 0.0017 ppm of OH^-.

Exercise 6

Since both the H^+ and OH^- are present in equal amounts, pure water is neutral.

Exercise 7

Because there are H^+ and OH^- in pure water - even in such extremely small amounts - it does conduct electricity. One of the objectives of this mini-course is to develop how this is measured.

Exercise 8

NaCl, H_2SO_4, KNO_3 are strong electrolytes - they are good conductors of electricity.

Exercise 9

Acetic acid, NH_4OH, HF are weak electrolytes - their aqueous solutions are poor conductors of electricity.

Exercise 10

Sugar, glycerine, alcohol are non-electrolytes - their aqueous solutions do not conduct electricity.

Exercise 11

We know that the reaction proceeds spontaneously, therefore the free energy must be negative.

Exercise 12 & 13

The precise, orderly crystalline structure of the NaCl has been destroyed, so the entropy has increased. (NOTE: This simple statement ignores attractions between water and the ions, but the conclusion is correct.)

Exercise 14

We note that there is little or no heat change when NaCl is dissolved in water. Therefore, the enthalpy change is negligible.

Exercise 15

Substituting these observations in the above equation:

Free energy = (small enthalpy) - (large entropy x $298^{\circ}K$)

Free energy = a negative quantity, the reaction proceeds spontaneously.

Exercise 16

$$K_{sp} = [Ba^{++}][SO_4^{--}] = 1.5 \times 10^{-9}$$

The solubility of $BaSO_4 = [S] = [Ba^{++}] = [SO_4^{--}]$

$$S^2 = 1.5 \times 10^{-9} = 15 \times 10^{-10}$$

or $S = \sqrt{15 \times 10^{-10}} = 3.4 \times 10^{-5}$ moles/liter

$$\frac{3.4 \times 10^{-5} \text{ moles } BaSO_4}{1 \text{ l.}} \times \frac{233 \text{ g } BaSO_4}{1 \text{ mole } BaSO_4} = 7.9 \times 10^{-3} \ \frac{\text{g } BaSO_4}{\text{l.}}$$

Exercise 17

$$E_3 = R_3I_1$$

Exercise 18

$$E_4 = R_2I_2$$

Exercise 19

$$R_3/R_2 = I_2I_1$$

Exercise 20

If $R_3/R_2 = I_2/I_1$ and from previous work $X/R_1 = I_2I_1$, then it follows that $X/R_1 = R_3/R_2$ or $X = R_3/R_2\ KR_1$.

Exercise 21

$$L = \frac{1}{0.833 \text{ ohms}} = 1.220 \text{ ohms}^{-1}$$

Exercise 22

k = specific conductance = cell constant X L

k = 0.01286 = cell constant x 1.220

cell constant = 0.01056

Exercise 23

$L = \frac{1}{1.267} = 0.7893 \text{ ohms}^{-1}$

k = 0.01056 x 0.7893 = 0.008335

Exercise 24

As the solution becomes increasingly dilute, fewer and fewer ions obstruct their path.

Exercise 25

(Answer on following page.)

Exercise 26

Actually, the best and most scientific definition of a strong electrolyte is one that gives a straight line when so plotted.

Exercise 27

The plotted curves tell us that strong electrolytes are better conductors of electricity than weak electrolytes.

Exercise 28

The equivalent conductance of the latter approaches that of the strong electrolytes at infinite dilution. These values have to be calculated as will be shown.

Exercise 29

Since it is the ions that conduct the electricity, acetic acid is a weak acid and NH_4OH is a weak base; HCl and NaOH are, respectively, a strong acid and a strong base.

Exercise 30

The above table also shows that H^+ and OH^- are by far the best conductors of electricity. With this data and our newly found understanding of equivalent conductance, we are now in a position to show how a most important constant is determined.

Exercise 31

$c = \frac{1,000}{18} = 55.3$ moles

Exercise 32

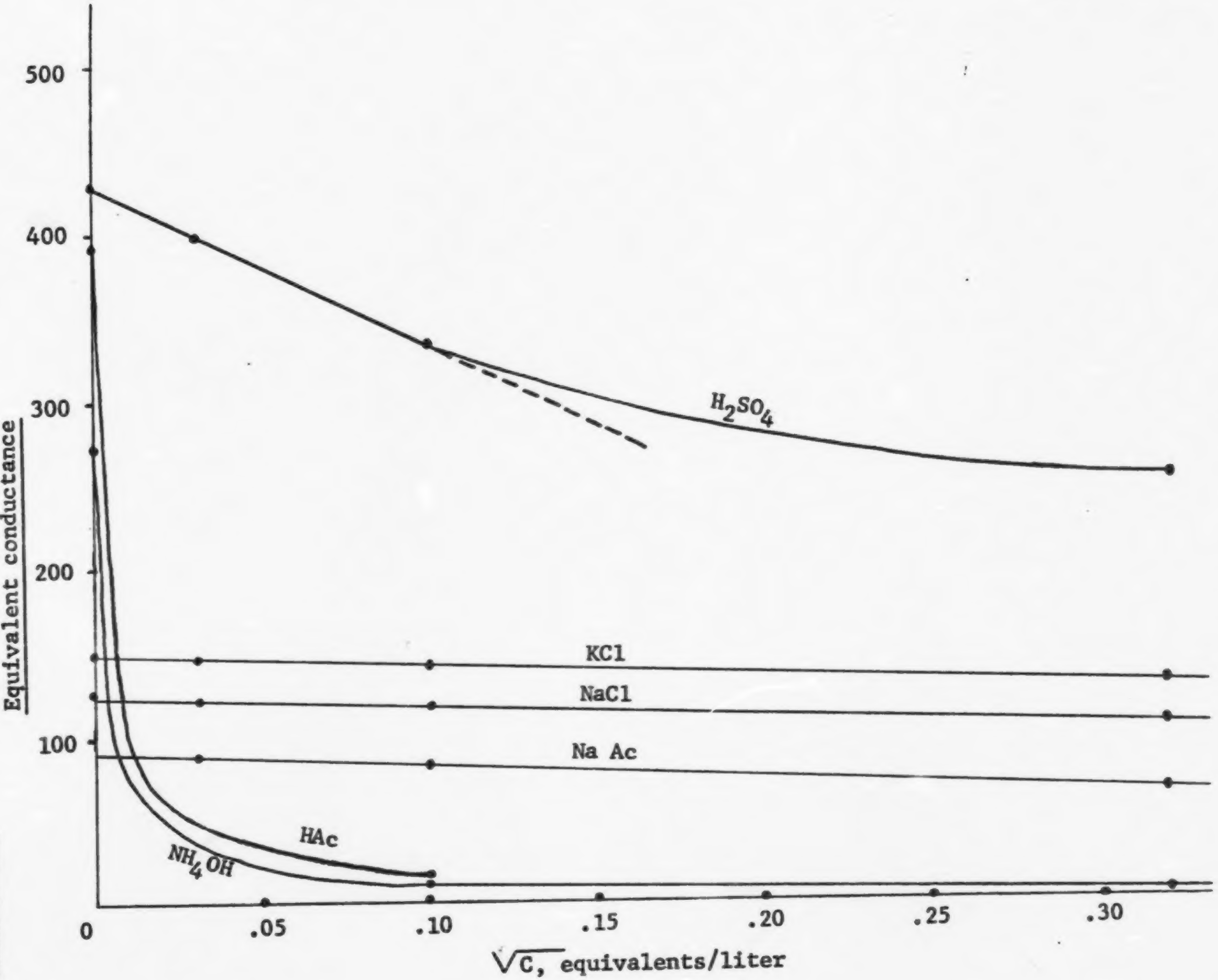
$$\Lambda = \frac{1,000 \times k}{c} = \frac{1,000 \times 0.50 \times 10^{-7}}{55.3} = 1.05 \times 10^{-6}$$

Exercise 33

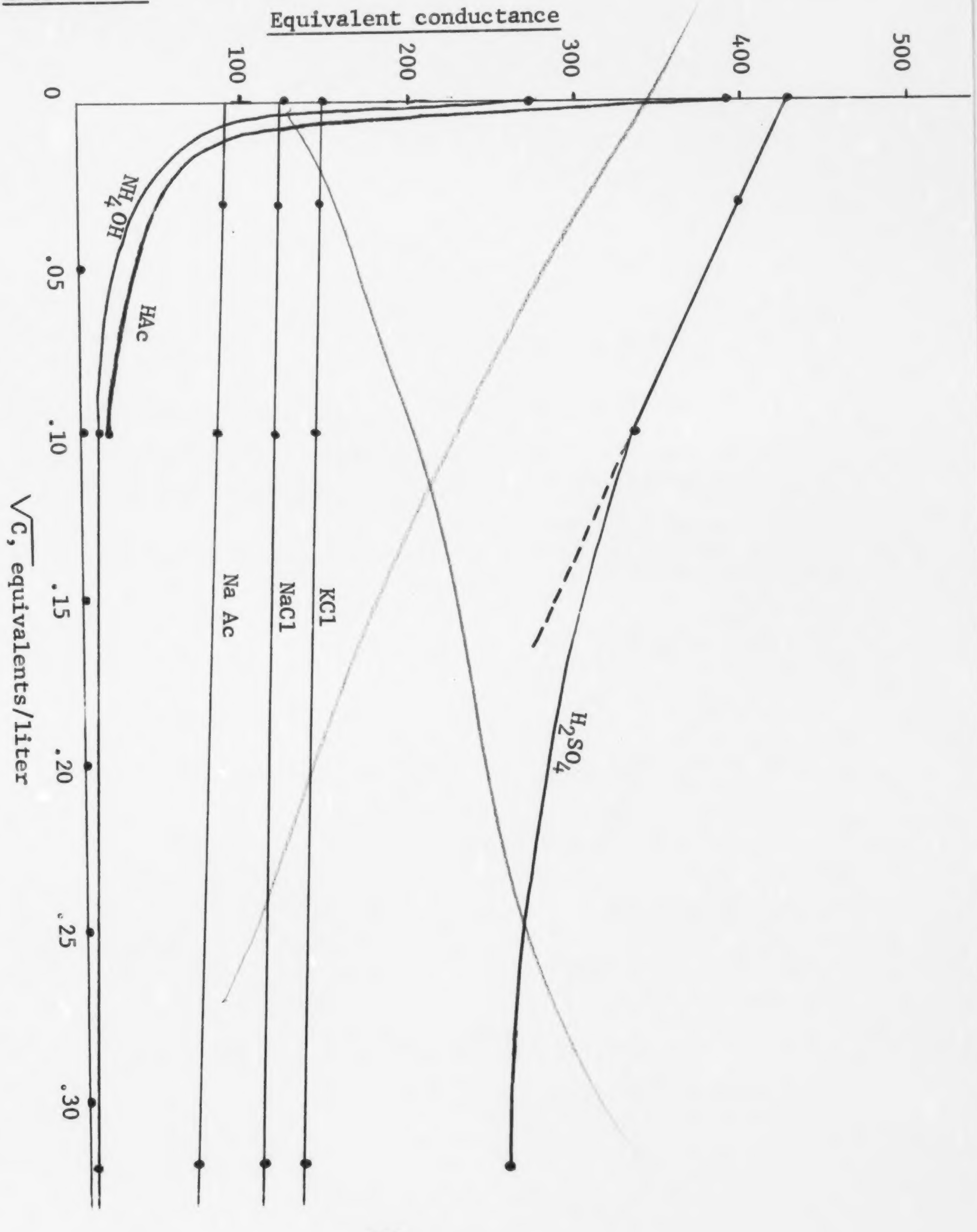
The equivalent conductance of H^+ = 349.82 and OH^- = 198.0, so the total equivalent conductance of water should be:

349.82 + 198 = 547.8, if it were totally ionized.

Exercise 25


Equivalent conductance
500
400
300
200
100
0
.05
.10
.15
.20
.25
.30
$\sqrt{c}$, equivalents/liter
H_2SO_4
KCl
NaCl
Na Ac
HAc
NH_4OH

Exercise 25


Equivalent conductance
0
100
200
300
400
500
.05
.10
.15
.20
.25
.30
$\sqrt{C}$, equivalents/liter
NH_4OH
HAc
Na Ac
NaCl
KCl
H_2SO_4

Exercise 34

$$1 : 547.8 :: x : 1.05\times10^{-6}$$

$$x = \frac{1.05\times10^{-6}}{547.8} = 1.9\times10^{-9}$$

Exercise 35

The molar concentration (c) of the H^+ and OH^- is:

$$c = 53.3\times1.9\times10^{-9} = 1\times10^{-7}$$

Exercise 36

Thus $[H^+] = [OH^-] = 1\times10^{-7}$ moles/liter

$$K_w = [H^+][OH^-] = 10^{-14}$$

Exercise 37

$$\Lambda = \frac{1{,}000\times k}{c}$$

$$c = \frac{1{,}000\times k}{\Lambda} = \frac{1{,}000\times125\times10^{-6}}{140} = 0.893\times10^{-3} \text{ equivalents/liter}$$

If we assume the salts average about 60g/equivalent, then:

$$c = 0.893\times10^{-3}\times60 = 54.6\times10^{-3}\text{g/l} = 55\text{mg/l} = 55\text{ppm}$$

Exercise 38

In this case, the charge carrying ions are discharged at the cathode but not at the anode.

Exercise 39

	Voltage	Multiply by
$2Fe^{++} \longrightarrow 2Fe^{+++}$	-0.771	-1

Exercise 40

$Cu \longrightarrow Cu^{++}$	-0.337	+1

Exercise 41

$$Cu + 2\,Fe^{+++} \longrightarrow Cu^{++} + 2\,Fe^{++} + 0.334 \text{ volts}$$

Exercise 42

The reaction occurs spontaneously.

Exercise 43

Wanted reaction $2\,Fe^{++} + Cl_2 \longrightarrow 2\,Fe^{+++} + 2\,Cl^-$

Half reaction	Voltage	Multiply by
$2\,Fe^{++} \longrightarrow 2\,Fe^{+++}$	-0.771	+1
$2\,Cl^- \longrightarrow Cl_2$	-1.3595	-1
$2\,Fe^{++} + Cl_2 \longrightarrow 2\,Fe^{+++} + 2\,Cl^-$	+0.588 volts	

A spontaneous reaction.

BACTERIA IN WATER

SUMMARY

The presence - or absence - of bacteria is one of the most important differences between polluted and potable water. Although the water chemist is usually not a bacteriologist, he must know enough about basic laboratory techniques so that he can run the necessary tests to establish this important parameter.

There are countless kinds of bacteria, a brief description of which is given from the point of view of good drinking water. These bacteria are classified and each class is briefly discussed. Although some bacteria are classified as non-pathogenic - that is, they do not causes diseases in man - drinking water standards demand that no bacteria are present in drinking water.

A detailed procedure is given for the determination of total coliform, fecal coliform and fecal streptococci in water.

ACKNOWLEDGEMENTS

The author is indebted to Dr. Joe F. Allen of Clemson University and Dr. Donald Wilkinson of Delaware State College for helpful suggestions regarding the format of this mini-course.

RATIONALE

Bacteria are classified in many ways. On completion of this mini-course, the student should be able to list and discuss these.

Bacteria are not always present in natural waters. Knowing when and where to look for bacterial contamination can be of critical importance.

On the other hand, some bacteria are allowed in swimming pools and other waters used by people. This is information that the water chemist must know about - and how to use it.

PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. Use a microscope.
2. Performdilutions to within ±1% using sterile pipettes and volumetric flasks without causing contamination.
3. Define buffer.
4. Use an autoclave.
5. Handle sterile equipment without causing contamination.
6. Use petri dishes and agar to grow colonies of bacteria.
7. Transfer membrane filters to agar dish without causing contamination.

OBJECTIVES

At the completion of this minicourse, the student should be able to:

1. Compare and contrast the action of aerobic and anaerobic bacteria upon pollutants in water. Included should be the chemical form of the products, the effect upon animal life in the water, and the general conditions of the water.

2. Define and classify bacteria as:
    - aerobic
    - anaerobic
    - faculative anerobes
    - bacilli
    - cocci
    - streptococci
    - staphylococci
    - spinella
    - Gram positive
    - Gram negative
    - spirochete
    - pathogenic
    - non-pathogenic

3. Identify from a group of drawings of pictures of microphotographs that which represents:
    - cocci
    - bacilli
    - spirilla
    - spirochete

4. State that coliform bacteria are used as the official indicator of water quality (USPHS), and discuss why this choice was made (five reasons).

5. Given the doubling time of a bacterium, calculate the approximate number of bacteria formed in a given time period (say, 24 hours).

6. Given the equipment and the procedure, analyze water samples for three different kinds of bacteria in water which are indicators of pollution.

7. Discuss the rationale during these tests for:
    - a. autoclaving
    - b. running a blank
    - c. refrigeration of samples

8. Given suitable data, calculate the bacterial count and conclude whether the water is safe for (a) drinking (b) swimming.

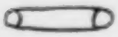
PRETEST

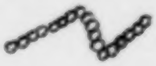
As a test of your knowledge before studying this mini-course, do this pretest Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this min-course as a learning tool.

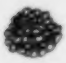
1. Which of the following are bacteria? (1) streptococci, (2) staphlococci, (3) bacillus, (4) spirilla, (5) all of these, (6) none of these.

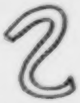
2. Which are harmful? (1) pathogenic bacteria, (2) non-pathogenic bacteria.

3. Label each of the following drawings as most likely: (1) streptococci, (2) staphlococci, (3) spirilla, (4) bacilli.

a. 

b. 

c. 

d. 

4. Which of the following bacteria help to clean water of undesirable organics? (1) pathogenic, (2) streptococci, (3) aerobic, (4) anaerobic, (5) Gram negative.

5. Discuss why coliform bacteria are used as the indicator of dangerous bacteria in water.

6. A bacterium has a doubling time of 45 minutes at room temperature How many colonies will grow from one original colony in 6 hours?

7. When analyzing for coloform, why is it necessary to:
   (a) run a blank?
   (b) antoclave?

8. A 10 ml sample of water from a stream measured 25 colonies without dilution and 2 colonies upon dilution 1:10. (a) What is the bacterial count? (b) Could this water be used for drinking? (c) Would you swim in this water?

REFERENCE

Fuller, Edward C., Chemistry and Man's Environment, Houghton Mifflin Co., Atlanta, 1974

BACTERIA IN WATER

Microorganisms are other all-important partners in the master plan of life on this wonderful planet we call earth. Yeasts, molds, fungi, bacteria and algae are inexplicably interwined in every phase and kind of living matter. Life, as we know it on earth, could not survive without the myriad microorganisms that inhabit the narrow domain slightly below the earth's surface to a small distance above it. Our attention is now focused on bacteria. A later Study Guide will be devoted to algae.

An introductory course in bacteriology is a year's work. As in the study of any major science a year is just the beginning; it merely whets the appetite of a serious student. Obviously, this one mini-course can only touch on a few high spots that are of particular concern to the water chemist.

About a hundred years ago it was possible for one person to know all there was to know of every science. Today, it is next to impossible to keep abreast of the new discoveries in one's chosen field of specialization. Thus, for many years, the scientist has endeavored to formulate general principles which embrace a large amount of isolated data and/or findings. Even though it seems to be a losing battle, this is the best he can do to minimize what would otherwise be an even more impossible task. For example, the chemist has devised many ways to group his knowledge so as to better comprehend the whole. Just to mention a few:

Exercise 1

Name several (at least six) chemical "groupings" of elements or compounds. (e.g., metals and non-metals.)

As in all processes regarding living matter, there must be a driving force to sustain and promote growth. This driving force is the release of energy. To live and multiply, bacteria must have a source of energy which they obtain by breaking down complex organic matter into simplier molecules. The most efficient method for deriving the largest amount of energy is for the bacteria to operate in the presence of oxygen - as we will presently see. Such bacterial action yields tremendous amounts of energy, hence proceeds spontaneously like water running down a steep hill. If oxygen is not present, Nature has devised other means of coping with the situation, so there are:

Aerobic and anaerobic bacteria

We have seen that some bacteria need oxygen to "eat" organic wastes, the products being CO_2 and water. Such bacteria - those that need oxygen for their proliferation - are known as aerobic bacteria. Given a fair chance, such bacteria cleanse our streams, rivers, and lakes. As will be seen later, one of the main objectives of a sewage treatment plant is to reduce the B.O.D. of the raw waste by the action of aerobic bacteria.

Exercise 2

What are anaerobic bacteria?

One has often seen bubbles breaking the surface of a stagnant pond or lake.

Exercise 3

What do you think the main component (gas) of these bubbles is?

Certain anaerobic bacteria may also produce H_2S, NH_3, and N_2 as the end products of their metabolism.

How fortunate we are that the above reactions take place! It means that Nature is combating pollution in the presence of and in the absence of dissolved oxygen in the water.

As we will see later, anaerobic bacteria are also called upon to carry out an important operation in most sewage treatment plants.

Believe it or not, there are some bacteria that grow either in the presence of or without oxygen. Such organisms are called facultative anaerobes

Exercise 4

(a) Which kind of bacteria would you expect to find in a malodorous (stinking) polluted lake or river, aerobic or anaerobic?

(b) Would you expect to be able to catch fish in a lake which has bubbles breaking the surface? Why or why not?

Pathogenic and non-pathogenic bacteria

There appear to be countless types of bacteria. Some are our best friends, others are deadly enemies. The pathogenic bacteria are those which cause such diseases in man and beast as:

Exercise 5

List a few diseases you know or suspect as being caused by bacteria.

One of the great advances of modern science is the growing understanding of bio-medical research which has done so much to combat many of these dread diseases.

Exercise 6

Are non-pathogenic bacteria harmful?

Exercise 7

Name some useful applications of non-pathogenic bacteria.

Bacilli, Cocci, and Spirilli

Bacilli are rod-shaped bacteria. Under a microscope they look like a pencil or a short rod. This, however, is easier to say than to demonstrate. Most bacteria are so small that they can only be seen with the aid of a high-power microscope at magnifications of 1000x to 1500x. This is the limit of magnification possible with visible light.

Gram positive and Gram negative bacteria

Gram is the name of a Danish scientist who discovered that some bacteria, after being stained with crystal violet and iodine, retain the color of crystal violet after being washed with ethanol. Such bacteria are said to be Gram positive; those which do not retain the crystal violet color after going through the same procedure are called Gram negative.

In the treatment of certain diseases, it is helpful to the physician to know whether the bacteria is Gram negative or Gram positive since the former are killed or inhibited by sulfa drugs and penicillin, whereas the Gram negative bacteria are affected only slightly by these drugs.

All bacteria are either Gram positive or Gram negative. This test, then, divides them into two broad catagories just as the chemist might divide solutes into electrolytes and non-electrolytes. Other observations are made as to the bacteria's shape, appearance in large colonies, mobility, comparison with known strains of pure cultures, etc., and etc., all of which narrows the field thus enabling the skilled bacteriologist to possibly identify bacteria responsible for a fish kill, or a sick baby, or a dead cow, or a sore throat.

Streptocci and Staphylococci

Cocci are grouped in a variety of ways, the two most commonly referred to being:

1. Streptocci, which means that the spherical bacterial cells are formed into rows of cells like a chain of a string of beads.
2. Staphlococci appear as irregular clusters resembling a bunch of grapes.

These then are other bits of information which help the bacteriorlogist identify an unknown bacteria.

In general, bacilli do not occur in the variety of patterns characteristic of cocci. Occasionally they do appear in pairs (diplobacilli) or chains (streptobacilli).

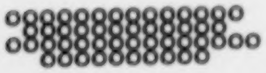
Spirilla occur predominantly as unattached individual cells.

Cocci are spherical bacteria. There seems to be no relationship between the shape of a bacteria - whether rod or spherical - as to whether it is pathogenic or non-pathogenic, aerobic or anaerobic.

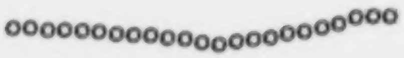
Spirilla are curled or spiraled bacteria. Some of these are extremely pathogenic and are resistant to drugs and medicines. On the other hand, our saliva is loaded with spirilla that help to begin the digestion of the food we eat.

Exercise 8

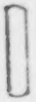
Label the following drawings as best represents cocci, bacilli, or spirilla.



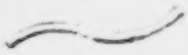
A ______________________



B ______________________



C ______________________



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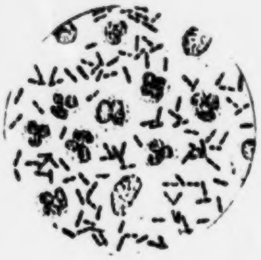
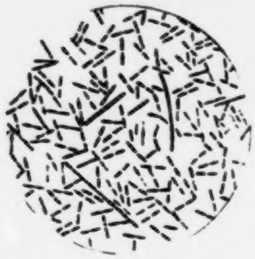
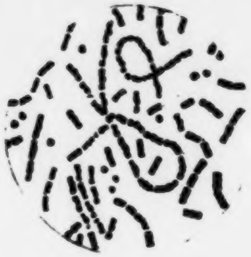


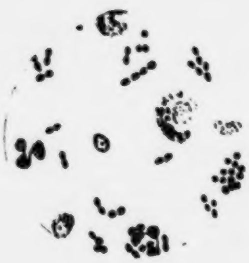
E. Coli
bacillus



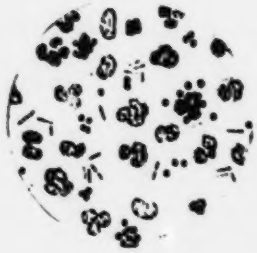
Typhoid
bacillus



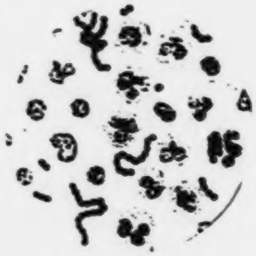
Strepto
bacillus



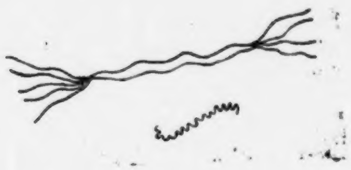
Coccus



Staphylo-coccus



Strepto-coccus



Spirochete

A Few Factors Influencing Bacterial Growth

Exercise 9

Discuss how the following factors might influence bacterial growth:

(a) Nutrients:

(b) Temperature:

(c) pH:

ANALYZING WATER FOR COLIFORMS

The bacteriological quality of water subject to federal control is governed by the U.S. Public Health Service Drinking Water Standards. These regulations stipulate that members of the coliform group are the official indicators of the bacteriological quality of a water. The regulations further state that the procedures used must be in accordance with the latest edition of "Standard Methods for the Examination of Water and Waste Water".

Coliforms were selected as indicators of human and/or animal fecal pollution because they are present in very large numbers in the feces; they tend to survive outside the body for a fairly long time; they are non-pathogenic; they are easy to isolate and identify and they exist under similar conditions with the enteric pathogens. (Enteric: pertaining to the intestinal canal.) Therefore the presence of coliforms in water constitute a health hazard not because they are dangerous but because they indicate the possible presence of enteric pathogens such as typhoid fever, dysentery, and cholera. Consequently, sanitary standards for drinking water are based on the concentration of coliforms since they exist under similar conditions with the enteric pathogens.

In well water or raw water the total coliform count does not give a true index of the quality. Thus the need for tests to differentiate Fecal Coliform and Fecal Streptococci is deemed necessary. Fecal coliform are more susceptible to salinity and chlorination than fecal streptococci; on the other hand, fecal streptococci are less tolerant to soil environment than fecal coliform. These tests can give the recency and source of pollution, since they are based on the life span of the bacteria involved.

Exercise 10

As a brief review, what are the advantages and disadvantages of using fecal coliform as the indicator of human wastes?

Although most states are guided by Federal standards, there are some variations due to local autonomy. Many states require that water must at least meet the following standards:

	Total Coliform
Drinking water	1 per 100ml
Chlorinated swimming pools	1 " "
Shell fishing	70 " "
*Flow-thru lakes and ponds	2400 " "

*If fecal coliform is greater than 400 colonies per 100ml, then the water should be re-sampled and the count average less than 200 colonies per ml for five consecutive samples taken over a period not exceeding thirty days.

If in any one sample the fecal coliform count is greater than 400 colonies per 100ml, the water is watched closely and resampled immediately. Or, dangerous conditions are indicated if the fecal coliform count averages more than 200 colonies per 100ml for five consecutive samples taken over a period not exceeding thirty days. Under either of these circumstances, the health authorities keep a watchful eye on the lake or pond and close if it deemed necessary.

Exercise 11

A disease is sweeping the country. You find the disease is caused by bacteria, so you run tests to determine the characteristics of the bacteria. It is found to be Gram positive, anaerobic streptococci which arepsychrophilic and acidophilic.

(a) Is the bacterium pathogenic?

(b) Identify, by letters, the bacterium below most likely to cause this disease.

(A) Grows best when cold in neutral aqueous solution, stains violet and looks like

(B) Grows best when cold in acid solution, does not stain and looks like

(C) Grows best when cold in acid solution, stains violet and looks like

(D) Grows best when hot in basic solution and looks like

Exercise 12

(a) Large quantities of fecal bacteria are discovered in a well found in an area to have salinity in the water. Are the bacteria to be fecal coliform or fecal streptococci?

(b) If local wells are found to contain considerable amounts of fecal coliform, are the coliform dangerous? Would you drink the water?

There are two accepted methods of coliform bacterial identification in water:

(1) Multiple tube fermentation, and

(2) Membrane filter.

Both of these methods are contained in Standard Methods, but the membrane filter technique is usually preferred. When a sample of water is passed through the filter, microorganisms larger than the filter pore size (0.45 microns) are held on the filter for subsequent culture to form visible colonies. The theory behind this is as follows:

As previously stated, bacteria are so small that they can only be seen with the aid of a high-powered microscope. But under optimum conditions - such as listed above - one bacterium divided to become two in 20 minutes, four in 40 minutes, eight in 60 minutes, etc. This may not seem to be very rapid growth, but is sure is. Here's why.

In doubling every 20 minutes, this means that we have $2^3 = 8$ bacteria produced in one hour. Thus in a day one molecule produces $2^{3x24} = 2^{72}$ bacteria. The best way to solve this is to let:

$$y = 2^{72}$$

$$\log y = 72 \times \log 2 = 72 \times 0.301 = 21.672$$

$$y = 4.7 \times 10^{21}$$

In just 24 hours one bacterium has multiplied to produce over a thousand billion billion bacteria. Such a colony is so large that it can be easily seen with the naked eye. As a matter of fact one must, from experience, dilute a water sample until the number of colonies formed on the filter can be accurately counted. If there are too many, they overlap so that the results are uncertain; if there are too few colonies, the results are likewise discarded.

Exercise 13

(a) How many bacteria would be formed in 24 hours if the temperature warms up and the bacteria divided every 15 minutes rather than every 20 minutes?

(b) Do the same calculation in a cooled speciman for which the division time is 30 minutes.

(c) Why are some foods, especially ground meats, always stored in refrigerators?

TOTAL COLIFORM

Equipment and materials

(1) Autoclave
(2) Incubating oven
(3) Balance
(4) Sterile plates
(5) Sample bottles - 250ml wide-mouth glass-stoppered
(6) Dilution bottles - graduated milk dilution bottles with screw cap; 160ml with line at 99ml
(7) Pipettes - 10ml
(8) Membrane filters
(9) Forceps
(10) Vacuum flask
(11) Gelman Parabella filtration funnel
(12) Vacuum source
(13) 95% ethanol or absolute methanol
(14) Bunsen burner
(15) Magnification unit for plate counting

(16) Hot plate
(17) Graduated cylinders - 100ml
(18) Agars and appropriate media
(19) Constant temperature water bath
(20) Buffered dilution water
(21) Brown wrapping paper
(22) Magnetic stirrer-hot plate combination
(23) Buffered water for rinsing - 350ml in 500ml Erlenmeyers

Sterilizing equipment and supplies

Everything should be sterilized the day before they are to be used. Items that are wrapped in brown paper should be covered thoroughly, the paper overlapped generously, Scotch tape used to hold paper in place so there is no chance of contamination after removal from the autoclave.

Dry equipment

Wrap each filter funnel unit (stainless steel Gelman Parabella filtration funnel) separately in brown paper - shopping bags work very well.

Wrap each graduated glass cylinder separately in brown paper.

Wrap pipetttes in groups of ten in brown paper, be sure that all tips point the same way, and mark paper as to tip end; or put the pipettes in an aluminum pipette holder, tip end down, and cushion the bottom of container with a mat of cotton.

Be sure to insert a strip of brown paper between the stopper and the bottle neck to prevent sticking. Bottles for water samples are covered with a generous piece of aluminum foil and firmly crimped around the neck.

All of the above can be autoclaved together at 121° C. (15 lbs. pressure) for 20 minutes. Quickly release the pressure and remove items from the autoclave; this prevents paper from getting wet and soggy. If this should happen, everything must be rewrapped and again sterilized.

Water solutions

Measure 93ml of buffered water into each milk dilution bottle; snugly screw on cap equipped with non-toxic liner; unscrew one turn before placing in autoclave. This prevents exploding while being autoclaved. (About 2 to 5 bottles are needed per sample.) Avoid crowding when positioning the bottles in the autoclave.

Rinse water is also made with the same buffered water. About 350ml are poured into 500ml Erlenmeyer flasks which are then covered with a generous square of aluminum foil crimped tightly around the neck of the flask.

Autoclave the above for 15 minutes at 121° C (15psi) once temperature is reached. At the end of this period, start a slow release of pressure so as to prevent bursting of bottles or water blowing out of the bottles. If any bottles are broken or the tops dislodged, they must be discarded.

Exercise 14

From past studies in this and other mini-courses, you should be able to give explanations for the following:

(a) Why is it bad for the paper to get wet after autoclaving?

(b) During autoclaving, why must caps of the bottles be loose? What could cause an explosion?

(c) After autoclaving the water solutions, why must pressure be reduced slowly?

(d) Why is "buffered" water used rather than plain, pure water?

(e) Why are the necks of the Erlenmeyer flasks crimped tightly with aluminum foil?

Preparation of culture media for total coliform

It is good practice to cover the work bench top with fresh brown paper to insure against contamination from the previous day's work.

Weigh 6.2g. of dehydrated M-Endo broth (or the equivalent) plus 1.5g. of agar in a clean 250ml Erlenmeyer flask, add 100ml of distilled water, and stir continuously while heating to a definite boil but do not boil more than one minute. Be sure not to scorch; a Teflon covered magnetic stirrer is recommended, coupled with a hot plate. Immediately remove from the heater, and soon thereafter pour about 5 to 6ml into autoclaved or sterile petri dishes. Allow the agar to solidify; as soon as possible put on cover and immediately invert, but be sure that agar is hard enough to not flow onto lid.

These can be used immediately if samples are available. Otherwise place the inverted petri dishes in a covered box and store in a clean refrigerator at 4° to 10° C. No organic chemicals should be in the refrigerator.

Exercise 15

It is really necessary to store the agar dishes in a refrigerator?

Taking samples

About 200 ml of sample are poured into the carefully labeled sterile sample bottles leaving an air pocket of about 50ml. The bottles should be packed in ice enroute to the laboratory, and the bacteriological analysis started as soon as the samples arrive. If possible, the time between sampling and delivery to the laboratory should be no more than one hour - never more than 24 hours.

If the sample has been chlorinated, then sterile $Na_2S_2O_3$ must be added - see "Standards Methods".

Exercise 16

What is the purpose of adding $Na_2S_2O_3$?

Procedure

With the work bench covered with fresh brown paper, the following must be assembled and ready for use before the sample arrives:

Filter funnel assembly with filter flask and source of vacuum.

Sterile milli-pore filters.

Rounded tip forceps; no corrugations on inside of tip.

A small beaker containing 95% ethanol.

Bunsen burner.

Milk dilution bottles containing sterile buffered water.

Sterile rinse water.

Sterile pipettes.

Agar filled petri dishes, carefully labeled: sampling location, sample size and other pertinent information.

Experience will soon result in the most convenient arrangement for the above.

As soon as the samples arrive in the laboratory, place them before an appropriate row of dilution bottles, open the package of pipettes (not the tip end) and make a series of dilutions based on the history of the sample; use sterilized distilled water in the milk dilution bottles. Each dilution bottle should be shaken 25 times before the next dilution is made. In almost all cases, dilutions are made in steps of 1/10.

Unwrap the stainless steel filter funnel and place in filter flask. Take forceps from the ethanol, flame the tips a few seconds, place a sterile membrane filter grip side up on the center of the filter support, and lock the top of the funnel in place; be sure not to tear the filter; discard if torn. Wet the membrane with a few mls of sterile buffered water, turn on vacuum, and add about 30ml of sterile buffered rinse water-this is the blank. Unlock the funnel top, start to remove the membrane with sterilized forceps, and turn off vacuum. This assures removal of excess water, which might lead to colonies of bacteria smearing across the membrane. If an air bubble occurs between the filter and the media, it must be removed before incubation; this is done by carefully raising and replacing the membrane with forceps. Immediately place membrane filter onto an agar filled petri dish, cover, invert and mark "blank".

Repeat the above procedure using the actual samples from the various dilution bottles - carefully mark each dish, always use sterilized forceps for handling the membranes. Almost always 10ml of the water sample is added using a sterilized pipette; tip of pipette should be held just above but not touching the membrane or side of filter. After sample has been added, turn on vacuum. After all the sample is drawn through the filter, rinse with three separate portions of sterile buffered distilled water. Unlock filter funnel and place membrane onto an agar filled petri dish-as above.

The above is repeated for all dilutions.

All the inverted petri dishes are placed on enamel trays which are lined with water-soaked paper towels. These trays are placed in an incubator maintained at 35° C. + 1°C. and greater than 90% humidity. After 24 hours + 2 hours of incubation, the plates are removed and the colonies counted using a binocular wide-field dissecting microscope at 10x to 15x magnification. The light source must come from above and perpendicular to the membrane's surface. All colonies are counted which are pink to dark red and must have a metallic sheen: the sheen may or may not cover the whole surface of the colony.

Each sample must be done on three aliquots or duplicate samples "TNTC" is written if the colonies are "too numerous to count", this means the colonies are so numerous that their growths overlap.

To be able to count properly, the total number of coliform colonies whould be between 20 and 80 per plate.

Exercise 17

Everything was sterilized, so why do we keep insisting that you run a blank?

FECAL COLIFORM

Equipment and materials

Same as for total coliform, except the addition of:

(1) water bath maintained at 44.5° ± 0.2° C.

(2) water-tight plastic bags for enclosing the petri dishes.

(3) Rosalic Acid.

(4) 0.2N NaOH

(5) M-FC broth

Sterilizing equipment and supplies

Same as for total coliform.

Preparation of culture media

To a 250ml Erlenmeyer flask containing 100ml of deionized distilled water, add:

3.7g. of M-FC media

1.5 of bacteriological agar

1ml of rosalic acid solution; this is made by adding 0.1g. rosalic acid to 10ml of 0.2 N NaOH.

Stir constantly while heating to boiling. As soon as the boiling point is reached, remove immediately from the hot plate, and pour 5 to 6ml of the media into petri dishes. When the agar has solidified, cover the petri dish and invert.

If not used immediately, place the inverted petri dishes in a box and store in a refrigerator free of organic vapors.

If used immediately, cover with a cloth to prevent light deterioration.

Procedure

If both total and fecal coliform tests are made, the fecal coliforms should be run first.

The procedure is exactly the same except that different culture media are used and the incubation is more precise. As with total coliform, the first and last samples are blanks consisiting of sterile distilled water. Remove air bubbles from under membranes.

A timer is set for 20 minutes when the first innoculation is made. At the end of this time, the inverted petri dishes are placed in water-tight plastic bags - no more than 7 to a bag. These are then submerged totally in a water bath maintained at 44.5° C. ± 0.2° C. This must not take more than 10 minutes, for a total of 30 minutes. With experience, several bags will be ready within 20 minutes. A blank should be run for each such batch.

It isn't easy to place weights on plastic bags so that they remain submerged. Thus it is recommended that each plastic bag be placed in a plastic Tupper Ware type of container with a tight-fitting lid. The bottom, top and sides of the plastic container should be perforated with holes to allow ready flow of water through the container. Be sure not to crowd the bags in the container or the containers in the water bath.

All samples are incubated 24 ± 2 hours.

Fecal coliform colonies are blue in color; only these are counted. Most fecal coliform colonies are much larger than total coliform colonies.

A good plate should contain 20 to 60 colonies.

FECAL STREPTOCOCCI

Equipment and materials

Same as for total coliform.

Sterilizing equipment and supplies

Same as for total coliform.

Preparation of culture media

To a 250ml Erlenmeyer flask containing 100ml of deionized, distilled water add 4.2g. of M-enteroccus agar. Heat, stir, use or store exactly as stated for fecal coliform procedure.

Place petri dishes in trays, cover with damp towels, and incubate at 35° C. ± 0.5° C. for 48 ± 2 hours.

The fecal streptococci colonies are medium to dark red. Do not count pink or clear colonies. The most accurate counts are taken from plates having 20 to 80 colonies per plate.

Exercise 18

In the following tests, 10ml of water, at the dilutions indicated, were put through a millipore filter, incubated, and examined for total coliforms.

(A) A sample of well water was tested (a) "as is" and at a (b) 10/1 dilution. It was found that the counts were (a) 15 and (b) 2. What is the bacterial count of the water? Is it safe for drinking?

(B) A pond used for swimming was sampled and the water diluted 1/10, 1/100, 1/1000. The 1/10 was 76; the 1/100 had a count of 11; the 1/1000 count was 0. What is the bacterial count? Is it safe for swimming?

(C) A stream was known to be polluted, but no one knew how badly. So you made the first test. Dilutions of (a) 1/10, (b) 1/100 and (c) 1/1000 were made. The 1/10 was TNTC; the 1/100 count was 55; the 1/1000 was 4. What is the bacterial count?

ANSWERS

A. Pretest

1. (5)
2. (1)
3. a = (4); b = (1); c = (2); d = (3)
4. (3)
5. See page 230.
6. 2^8 or 256 colonies.
7. a. the blank checks on your ability to keep samples sterile.
   b. the autoclane sterilizes all the equipment being used.
8. a. between 200 and 250 colonies per 100 ml.
   b. not safe for drinking.
   c. borderline for swimming - should be retested frequently.

B. Study Guide

Exercise 1

(a) Electrolytes vs. non-electrolytes

(b) Organic and inorganic compounds

(c) Substances that are soluble and insoluble in water.

(d) Gases, liquids and solids.

(e) The Periodic Table.

(f) Conductors and non-conductors of electricity.

(g) Toxic and non-toxic compounds.

(h) Acids and bases

(i) Crystalline and amorphous solids.

(j) Exothermal and endothermal reactions.

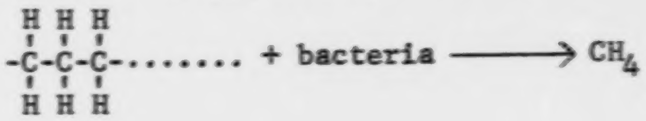
In a similar manner and basically for the same reasons, the bacteriologist has classified bacteria in numerous ways.

Exercise 2

Anaerobic bacteria are those which grow and multiply in the absence of air, while still deriving their energy from the organic matter they act upon.

Exercise 3

These gas bubbles are primarily methane:



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\cdots\cdots + \text{bacteria} \longrightarrow CH_4$$

Exercise 4

(a) Anaerobic.

(b) No. A heavily polluted stream with bubbles breaking the surface is indicative of anaerobic bacteria - hence lack of oxygen. No oxygen, no fish.

Exercise 5

Pneumonia, syphilis, gonorrhea, typhoid fever, hoof and mouth disease, strep throats, bubonic plague, trichinosis, lockjaw, anthrax, cholera, diptheria, tuberculosis, leprosy, whooping cough - just to mention a few.

Exercise 6

No.

Exercise 7

Non-pathogenic organisms can be and often are mankind's best friends. As noted in a previous mini-course, our digestive tract is loaded with many kinds of bacteria that promote the break-down of the food we eat into fragments small enough to pass through the walls of our intestines and thus enter our blood stream. Myriads

Exercise 7 - (con.)

of friendly bacteria populate the milk we drink; pasteurization is designed to kill any pathogenic organisms. As noted before, bacteria play a major part in combating water pollution. Fertile soil teems with bacteria that reduce organic matter into molecules small enough to enter the "blood stream" of vegetation. Bacteria produce enzymes turn grape juice into wine or vinegar, milks solids into cheese; they help convert raw hides into leather and flax into linen.

Exercise 8

(a) Staphlococci

(b) Streptococci

(c) Bacillus

(d) Spirilla

Exercise 9

(a) Nutrients

By far the most important factor influencing bacterial growth is the food fed to the bacteria. As will be evident in the following tests, the nutrient media specified for each type of bacteria being sought, is quite different and carefully designed to promote the growth of a particular type of bacteria, while discouraging the growth of others. The most careful adjustment of nutrients cannot, however, do it all. Therefore the bacteriologist incorporates other factors into his test which tend to promote the growth of the bacteria he is looking for. The development of new techniques and the refining of older ones are never ending challenges to the bacteriologist, just as new and improved analytical techniques are important to the chemist.

(b) Temperature

Bacteria seem to have the ability of accommodating themselves to their surroundings. In other words, some bacteria thrive and multiply under conditions that prevent or inhibit the growth of other bacteria. A good sample of such accommodation is bacterial response to temperature changes. Three groups are recognized:

Psychophilic (cold-loving) grow best at 10-15° C.

Mesophilic (moderate-loving) grow best at 25-37° C.

Thermophilic (heat-loving) grow best at 50-60° C.

(c) pH

Most bacteria prefer an environment that is nearly neutral, and culture media are usually adjusted or buffered to maintain a pH that is close to 7.0. However, there are the acid-loving (acidophilic) and the alkali-loving (alkaliphilic) bacteria which grow under these otherwise inhospitable conditions.

Exercise 10

Review the paragraph just before Exercise 10.

Exercise 11

(a) Yes.

(b) B

Exercise 12

(a) Fecal streptococci.

(b) Yes, they are dangerous.
No, don't drink the water.

Exercise 13

(a) $y = 2^{4x24} = 2^{96}$

$\log y = 96 \log 2 = 96 \times .301 = 27.692$

$y = 4.92 \times 10^{27}$

(b) $y = 2^{2x24} = 2^{48}$

$\log y = 48 \log 2 = 48 \times .301 = 14.448$

$y = 2.78 \times 10^{14}$

(c) To inhibit bacterial growth.

Exercise 14

(a) It would fall apart and probably allow bacterial contamination to infect the equipment.

(b) Expansion of the liquid and/or gas in the bottle might cause the bottle to explode.

(c) To allow for gradual equilization of pressure to take place.

(d) To maintain a pH that is best suited for the growth of bacteria.

(e) To prevent bacterial contamination.

Exercise 15

Yes, unless used immediately.

Exercise 16

To reduce Cl_2: $Cl_2 + S_2O_3^{=} \longrightarrow 2Cl^- + S_4O_6$

Exercise 17

Blanks are run on chemical analyses to assure that no accidental mistakes have been made.

Blanks are run on bacterial counts to make sure that everything was done properly, for there is always a chance that a human error slipped in the procedure.

Exercise 18

(A) (a) 150 colonies per 100ml

(b) 200 colonies per 100ml

The water is not safe for drinking.

(B) (a) 7,600 colonies per 100ml

(b) 11,000 colonies per 100ml

Probably not safe for swimming.

(C) (a) 55,000 colonies per 100ml

(b) 40,000 colonies per 100ml

ALGAE

SUMMARY

The nature of various forms of algae are discussed along with the role of algae in supplying O_2, removing pollutants, as a pollutant itself, and as a present and potential fuel supply.

RATIONALE

This mini-course should help you understand and appreciate the extremely important role of algae in regards to all living things. The meaning and wonder of photosynthesis should also help you to see life with amazement as to the simplicity - and extreme complexity - of one of Nature's greatest chemical feats.

But algae can also be a stubborn and almost deadly problem - many of our lakes, ponds and rivers are being threatened and slowly killed with extreme algal growths. What can the scientist do about this? What can you do about this? Could there be a more worthy objective than devoting a young life to such a study?

ACKNOWLEDGEMENT

The author is indebted to Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College, for helping to insert and answer the questions contained herein.

PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. Do stoichimetric calculations.

OBJECTIVES

At the completion of this mini-course, the student should be able to:

1. Define "algae" and discuss the role algae play: (a) in supplying the world with O_2, (b) as a potential source of food directly and indirectly, (c) as a pollutant in water, (d) as a major step in the aquatic food chain, (e) as an aid in small-scale water purification plants.

2. Define "photosynthesis" and state the requirements for photosynthesis, the role of chlorophyll in photosynthesis, and the results of photosynthesis upon algae.

3. Define an "algae bloom" and discuss the causes and effects of an algae bloom in a body of water.

4. Differentiate between Bentonic and Planktonic algae.

5. Differentiate between Green Algae, Golden Algae, Brown Algae, Red Algae, and Blue-Green Algae. Include where these may be found and at least one characteristic beyond the color.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. What are algae?

2. Algae and other sea-plants supply approximately what quantity of the world's oxygen? (1) <1%, (2) 5%, (3) 35%, (4) 75%, (5) <95%.

3. What algae are already in use as a food source for people?

4. The free-floating microscopic plants which provide much of the fish life of the ocean with food are: (1) kelp, (2) phytoplankton, (3) Golden Algae, (4) Brown Algae, (5) none of these.

5. Describe the causes and bad effects of an algal bloom in a body of water.

6. Why is photosynthesis in algae important to life on the earth?

7. What is the difference between bentonic and planktonic algae?

8. What are characteristics of Green Algae, Golden Algae, Brown Algae, Red Algae, and Blue-Green Algae? (Include where these may be found.)

9. Overall, are algae harmful or helpful? Why?

ALGAE

Quoting from the mini-course, This Good Earth, it was stated that:

> "During the earth's first billion years, ultraviolet light from the sun knocked hydrogen atoms out of methane and ammonia to form 'free radicals' of carbon and nitrogen atoms with one or two hydrogens attached: $CH^{\cdot}$, $CH_2^{\cdot}$, $NH^{\cdot}$, $NH_2^{\cdot}$ These are very active chemically and react with other constituents of the atmosphere to form a great variety of organic compounds. In this way, as the earth's oceans slowly grew, a rich stock of organic materials accumulated. When the earth was about a billion and a half years old, and after a billion years of chance combinations and accidental associations by processes not clear at present, the first primitive organisms were formed."

Chief among these 'first primitive organisms' were algae, which have the ability to produce oxygen by photosynthesis. Thus our present atmosphere gradually evolved over a period of four billion years

Algae are the prime source of oxygen on this planet; thus they are essential to all living processes. Algae were among the first of the primitive organisms formed in the earliest stages of the world's evolution Actually, the chemist does not usually determine algae in water as he frequently must do in the case of bacteria But algae can be a serious nuisance in blinding filters and causing unpleasant tastes in water.

Most biologists classify algae as plants since they contain chlorophyll; this is the green pigment that catalyzes the all-important reaction called photosynthesis. By this is meant the combining of CO_2, H_2O, and the sun's energy on the surface of a leaf or within the algae to produce food and release O_2.

Exercise 1

What are algae?

Exercise 2

What is photosynthesis?

As you should have brought out in your answers to Exercises 1 and 2, algae are plants, almost all of which live in water. Algae and green land plants undergo a series of reactions, which were referred to above, called photosynthesis. That is, they possess a green pigment (catalyst) called chlorophyll which enable all vegetation - aquatic and land - to combine the sun's energy with water and CO_2 to synthesize organic compounds and at the same time liberate O_2. We are well aware of the fact that these same three "raw materials" combine on the surface of leaves of land plants to become eventually on oak tree, tomatoes, corn, rice, grass, pineapples, and all other forms of vegetation when other nutrients are available.

In the oceans, lakes, rivers and streams, algae synthesize simple proteins, starches, and sugars which they store within their structures and then release oxygen into the environment:

$$CO_2 + H_2O + \text{energy} + \text{algae} \longrightarrow O_2 + \text{food}$$

Algae thus provides food for bacteria and other aquatic life. The protein content of some algae is more than 50% on a dry weight basis. Small fish feed on this and in turn become food for larger fish.

Thus a plant, because it contains chlorophyll, can synthesize food from: the sun's energy + CO_2 + H_2O. Algae do this in water and - it is estimated - account for about 75% of the O_2 in the atmosphere; land plants provide the remainder. It was algae, then, that were responsible for the gradual build-up of the O_2 in our atmosphere which now is about 80% N_2 and 20% O_2. Algae and land plants are constantly replenishing the world's supply of O_2 without which we would eventually suffocate.

This process known as photosynthesis is characteristic only of living matter that contains chlorophyll: algae and other green plants. It is not characteristic of animals. On the other hand, respiration is a process common to all plants and animals. Respiration is a gaseous exchange that is the opposite of photosynthesis; that is, O_2 is absorbed and CO_2 is released. However, with algae and other green plants, the rate of their photosynthesis is normally faster than their respiration. They release more oxygen than they use, and absorb more CO_2 than they release; animals and other non-photosynthetic organisms can only absorb O_2 from the environment and release CO_2.

Thus the amounts of oxygen and CO_2 in water often depend to a large extent upon the relative rates of photosynthesis and respiration being carried on collectively by the algae, bacteria, and other organisms in the water. Furthermore, since sunlight is essential to photosynthesis, algae are responsible for important chemical changes and metabolic activities in water due to their release of oxygen during daylight hours. For the water chemist, one practical result is the inhibition of foul conditions - which are characteristic of anaerobic bacterial action - by the promotion of aerobic bacteria.

Another important chemical effect of algae is the continuous removal of CO_2 from water during daylight hours as a result of photosynthesis. This process results in a change in the relative amounts of carbonates and bi-carbonates, often causing the latter to precipitate. This, in turn, changes the total hardness of the water. Vigorous algal growths may reduce water hardness by as much as one-third. (Water hardness will be the subject of another mini-course.)

Exercise 4

Would you expect photosynthesis to have an effect of the pH of water? Explain.

Obviously, algae are essential to life on this earth. They produce 75% of the oxygen in our atmosphere. But, like many other blessings, too much of a good thing can be a curse.

Exercise 5

What would be your impression of the problems caused by the following situations?

(a) Large algae blooms that cover the surface of a pond. What effects would this have on B.O.D., C.O.D., and D.O.?

(b) Large concentrations of phosphates and detergents that promote tremendous growths of algae.

(c) Often, large amounts of algae enter water treatment plants.

Let us not forget that this isn't the algae's fault. Actually, algal growth is Nature's way of making a valiant effort to remove contaminants from our water resources. It is up to us to remove these contaminants from our waste water before it is discharged into a lake, pond, or river.

Returning to the positive, algae that grow on the surface of a slow sand bed filter (often used for isolated, low-volume water supplies such as a restaurant on the Pennsylvania Turnpike) reduce its flow, but they perform a very useful service by removing bacteria and suspended solids, and by adding oxygen to the water.

To further accentuate the positive, the giant kelps of the ocean are algae which grow to be more than 150 feet tall and are harvested as a valuable crop. There are huge floating meadows of seaweed - algae - that are almost as large as a continent lying in the North Atlantic Ocean, Caribbean Sea, Gulf of Mexico, and Pacific Ocean. Actually, algae form the fundamental basis for ocean life since the larger fish live on the smaller ones, which ultimately feed on seaweed - algae.

Algae are found almost everywhere on the surface of the earth, and to considerable ocean depths. In some places where the snow never melts, algae are so so abundant that they color the snow red. On the other hand, algae grow in hot springs - such as in Yellow Stone Park - where the temperature is 85° C. Algae grow in the Great Salt Lake which is 15 times more concentrated in salt content than the Atlantic Ocean.

Exercise 6

As a review, list about three advantages of the presence of algae, and three potential disadvantages.

So far as is known, algae are not harmful to man or beast, though they do grow on the backs of turtles and other marine life. There is evidence, however, that algae cause serious damage to certain vegetation, particularly in the tropics.

The simplest algae are one-celled organisms. Many of these have thread like protrusions which propel the microscopic algae through the water; these protrusions are called flagelli. On the other end of the scale are the giant sea kelp.

Exercise 7

You have seen that algae are unique plants. Do you know how algae reproduce?

Like bacteria, algae are classified in many ways:

(a) Benthonic. These are submerged and attached to something underwater.

The predominant benthonic algae appear as filaments, are green, and grow attached to stones, twigs and other objects. They are the chief inhabitants of streams, ponds, lakes, and swamps. Each individual body of water, however, will have its own characteristic species of algae.

(b) Planktonic. These are free flowing.

Planktonic algae are usually unicellular and do not appear as filaments.

As emphasized above, all algae contain chlorophyll. In addition to this green pigment, many forms of algae contain other pigments which give them their characteristic coloration.

Exercise 8

The following algae have been observed; classify them as bentonic or planktonic:

(a) sea-weed -- ___________

(b) microscopic plants floating in sea water -- __________

Green Algae

These have no other pigments which alter or mask their chlorophyll. Some green algae are found exclusively in fresh water; others are abundant in the ocean. One widely distributed green algae propers where there is a rich supply of soluble nitrogeneous compounds, for example where there are droppings of sea birds on rocky shores.

Golden Algae

A yellow to brown pigment combined with the green chlorophyll is responsible for the gold color. These are almost exclusively fresh water algae. Many possess flagelli, and most reproduce by the formation of spores.

Brown Algae

All brown algae are multicellular, many of which are quite complex. Some reproduce by forming spore cells, others sexually.

The giant sea kelps are brown algae.

Red Algae

Certain forms of red algae only grow in oceans and then rarely in water more than 100 feet deep; nearer the Equator, other forms are found at depths of 500 feet. Still other forms are restricted to clear, cool, swiftly flowing streams. None of the red algae attain sizes comparable to that of the huge brown algae. Red algae are of great importance in the formation of coral reefs; their bodies are heavily impregnated with lime.

Blue-green Algae

These are the algae that color the Red Sea; other forms are found in fresh water.

Exercise 9

Which ones of the above algae types would:

(a) be found in fresh water? - __________

(b) be found in sea-water? - __________

(c) be found in fresh streams? - __________

(d) are represented by giant sea kelp? - __________

(e) reproduce by spores? - __________

(f) are found near bird droppings? - __________

(g) are colored exclusively by chlorophyll? - __________

(h) possess flagelli? - __________

(i) are used as food source? - __________

ANSWERS

A. Pretest

1. Primative, aquatic, one-celled or multicellular plants that lack true stems, roots, and leaves but which contain chlorphyll.
2. (4)
3. Kelp
4. (2)
5. See answers to Exercise 4 on page 254.
6. Photosynthesis uses the energy of the sun to convert CO_2, water, and other nutrients into carbohydrates and O_2 in the atmosphere comes from sea-plants.
7. Bentonic algae have roots attached to something underwater and appear as filaments. Planktonic algae are free floating and are usually unicellular.
8. See page 252 of study guide.
9. Helpful. They create much O_2 and help clean up water, but can be bad in excess.

Study Guide

Exercise 1

The dictionary defines algae as any of various primitive, chiefly aquatic, one-celled or multicellular plants that lack true stems, roots, and leaves but contain chlorophyll.

Exercise 2

Photosynthesis is defined by the dictionary as the process by which chlorophyll-containing cells in green plants convert incident light to chemical energy and synthesize organic compounds from inorganic compounds, especially carbohydrates from CO_2 and H_2O, with the simultaneous release of O_2.

Exercise 3

a. $$1 \text{ ton } C_{12}H_{22}O_{11} \times \frac{12X \text{ Mwt of } O_2}{1 \times \text{Mwt of } C_{12}H_{22}O_{11}} =$$

$$1 \times \frac{12 \times 32}{1 \times 342} = 1.12 \text{ tons } O_2.$$

b. $\underline{H_2O}$

$$1 \text{ ton } C_{12}H_{22}O_{11} \times \frac{11 \times \text{Mwt } H_2O}{1 \times \text{Mwt } C_{12}H_{22}O_{11}} =$$

$$1 \times \frac{11 \times 18}{1 \times 342} = 0.58 \text{ ton } H_2O.$$

c. Photosynthesis can, indeed, make lots of carbohydrates (like sugars) while consuming great amounts of CO_2 and water. In addition, more weight of O_2 is produced than sugar in this instance. Since there are many millions of tons of algae in the world, they produce millions of tons of O_2 yearly. In addition, land plants also produce much sugars and CO_2.

d. The oceans are much larger than the land, so over 50% ($\sim$75%) of the O_2 is generated by sea-plants! (Now you may regard the oil spills in the ocean a more serious problem than before.)

Exercise 4

Yes. As would be expected, changes in the CO_2 content and hardness of water tend to change the pH. The pH increases as the algae promote photosynthesis activity during daylight hours. The pH then decreases at night when the algae are releasing CO_2 during respiration.

Exercise 5

(a) Large growths of algae are sometimes called blooms. There are frequent algae blooms that are so extensive that they discolor the water. Such blooms often cause fish kills because the massive accumulation of algae-covering acts as a barrier to the penetration of atmospheric oxygen and sunlight to the water beneath the algae. In addition, the fast growing algae quickly consume all the nutrients and die. The dead algae then decay, further decreasing the O_2 content and causing bad odors.

(b) Algae, like all living matter, need food for their growth. The prolific wastes of civilization - and particularly phosphates from detergents - promote the growth of massive amounts of algae in lakes, ponds, and rivers. These are particularly dangerous to large areas in the Great Lakes and other major bodies of water that border heavily populated parts of the nation. It has been estimated, for example, that 130 tons of algae per day flow into the Fox River, Wisconsin, from Lake Winnebago. The volume of algae in the Scioto River, Ohio, has reached more than 8,000 ppm. Algal counts for Lake Michigan at Chicago often mounts 4,000 organisms per ml; the White River in Indiana has had as many as 100,000 algae per ml.

(c) The chemist in a water treatment plant may well look upon algae as the most troublesome of the various types of nuisance organisms with which he has to contend, for they often clog sand filters thus reducing flow rates; they may also be the cause of undesireable tastes and odors in the water.

Exercise 6

Advantages include:

(1) Produce O_2 to sustain animal life.

(2) Provide food for sea animals such as fish.

(3) Potential large food source for land animals including man.

Disadvantages of excess amounts of algae include:

(1) Clog filters in water plants.

(2) Can deplete O_2 and kill sea life when excess growth of algae dies.

(3) Interfere with use of body of water such as a lake.

Exercise 7

Algae multiply:

(a) Like a vegetable by dividing into two or more parts.

(b) By means of spores.

(c) By sexual reproduction.

Exercise 8

Planktonic for (b) microscopic plants floating in sea water, and, Bentonic for (a) sea-weed.

Exercise 9

(a) Some green forms, almost all golden, no brown algae, some red, some blue-green forms.

(b) All forms can be found in sea-water.

(c) Only red algae forms are found in streams.

(d) Brown algae.

(e) Most Golden, some brown.

(f) One form of green algae.

(g) Green algae.

(h) Some forms of all these have flagelli.

(i) Brown algae (kelp) are used as food sources.

THE CARBON CYCLE

B.O.D. C.O.D.

SUMMARY

This mini-course discusses the phenomena of biological oxygen demand (B.O.D.) and chemical oxygen demand (C.O.D.), gives the procedure for determining B.O.D. and C.O.D., and contrasts the two methods.

RATIONALE

Much of the material contained in the foregoing Study Guides will be called upon as the practical aspects of water chemistry is now introduced. The carbon cycle is one of nature's most important phenomena; in many cases - until the carbon cycle is completed - our civilization is confronted with pollution. B.O.D. and C.O.D. are one quantitative measure of this pollution.

ACKNOWLEDGEMENT

The author is indebted to Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College, for his help and advice in posing and answering many of the questions that follow.

PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. Define oxidation and reduction, and balance an equation using oxidation-reduction techniques.
2. Prepare solutions of the appropriate concentration when given the chemicals needed and the preparation procedure.
3. State reasons for using very clean glassware in solution preparation.
4. Do concentration and dilution calculations using molarity, normality, and parts per million.
5. Convert from parts per million to molarity and vice versa.
6. Perform a titration.

OBJECTIVES

At the completion of this mini-course, the student should be able to:

1. Define: Biochemical Oxygen Demand (B.O.D.)
   Chemical Oxygen Demand (C.O.D.)
   Dissolved Oxygen (D.O.)
   Carbon Cycle
2. State when the B.O.D. test probably originated.
3. Use a specific example (say manure) to trace the carbon through one carbon cycle.
4. State that the D.O. decreases as the temperature increases, and state why this is so.

5. Write a typical reaction of an organic compound being oxidized under the influence of bacteria.

6. Use a D.O. table and a given weight of sewage sample with a known B.O.D. to calculate the volume of water required to clean this sewage sample.

7. Given a redox equation, calculate the equivalent weight of the oxidizing and reducing agent.

8. Given appropriate data, calculate the B.O.D. and/or C.O.D. of a sample of water.

9. Perform three B.O.D and three C.O.D analyses to within ±10%, using appropriate reagents and a copy of the procedure.

10. Discuss the merits of B.O.D. and C.O.D. tests, including advantages and disadvantages of each.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. Trace a sample of animal waste through one complete carbon cycle.

2. What happens to the D.O. in a given water sample as the temperature increases? D.O. (1) increases, (2) decreases, (3) doesn't change.

3. What would happen to the B.O.D. in a stream or lake when a sewage treatment plant overflows? The B.O.D. (1) increased, (2) decreased, (3) showed no change.

4. What would happen to the C.O.D. in the event described in #3? (1) increase, (2) decrease, (3) no change.

5. For a given sewage sample, which will show the greater oxygen demand? (1) C.O.D., (2) B.O.D.

6. Write a typical reaction showing the oxidation of organics by O_2 with bacteria.

7. Balance the equation:

$$C_{11}H_{22}O_{11} + K_2Cr_2O_7 + H_2SO_4 \longrightarrow CO_2 + H_2O + K_2SO_4 + Cr_2(SO_4)_3.$$

8. What is the equivalent weight of $K_2Cr_2O_7$ in the above equation?

9. Given the data below, calculate the B.O.D. of this sewage sample: 10 ml sample size, D.O. for the blank is 7.8 ppm, D.O. for the original sample was 3.3 ppm, and D.O. for the incubated sample is 5.1 ppm.

10. Calculate the C.O.D. from the sample data below: A 300 ml sample was digested with 10 ml of 0.25 N $K_2Cr_2O_7$, then titrated with 0.1 N ferrous ammounium sulfate. The blank required 24.92 ml of the Fe^{+2} solution and the digested sample required 6.89 ml of Fe^{+2}.

THE CARBON CYCLE

B.O.D. C.O.D.

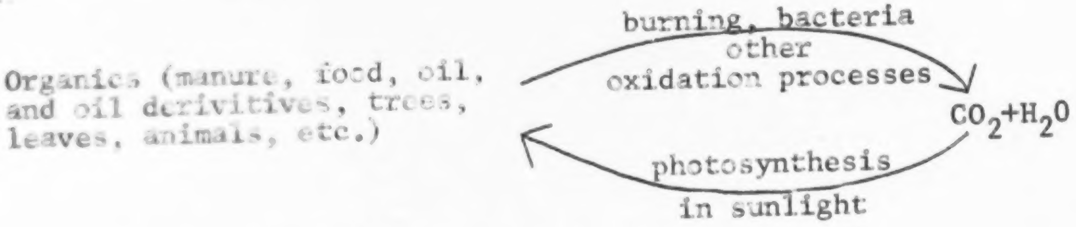
With the preceding Study Guides as a foundation, you are now ready to study the chemistry of water as applied to water purification and waste-water treatment.

Exercise 1

What do you think is meant by the carbon cycle?

The carbon sycle is one of the most important phenomena - if not the most important one - in the world. Without it, life on this earth, as we know it, would not be possible. It recalls a story that may well be factual, of a conversation between two neighborly farmers. The one believed in God and went to church; the other claimed to be an atheist. The God-fearing farmer asked his neighbor to accompany him to church next Sunday. The atheist said he would go, if his friend could prove to him that there was a God. Without hesitation, a big, strong, weather-beaten finger pointed to the ever present manure pile. "That," said the church-going farmer, "is my proof of God. Who else but God could have figured out what to do with it."

How much of the wonders of nature we take for granted! Not the least of these is the miracle of organic growth. How amazing it is that two simple gases - CO_2 and H_2O - together with energy from the sun combine as the surface of a green leaf to produce an oak tree, peas, roses, tomatoes, corn, wheat, rice and all other vegetation. This is, shall we say, the beginning of the carbon cycle.



Organics (manure, food, oil, and oil derivitives, trees, leaves, animals, etc.)
burning, bacteria other oxidation processes
CO_2+H_2O
photosynthesis in sunlight

FIG. 1 - THE CARBON CYCLE

The food so produced is eaten by beast and man. Energy and substance is derived from the food, but that which cannot be utilized forms the manure pile or domestic sewage. Spread upon the ground, bacteria act upon the waste until it can be assimilated by vegetation, thus producing more food and thereby starting another round of the carbon cycle.

Bacteria also act upon domestic sewage and convert it to CO_2, which is then freed, making possible another carbon cycle. The complexity of what happens on the surface of a leaf may never by unraveled by the ablest of scientists, but there is one step in this wonderful process of the carbon cycle that the water chemist must aid and assist.

If and when the manure is assimilated by plant life, and the organic matter in domestic sewage is converted to CO_2, our land and our water is no longer polluted - with such exceptions as phosphates, inorganic contaminants, and non-biodegradable organic wastes. Needless to say, these exceptions are often considerable and crucial; some will be the subjects of subsequent study guides.

The B.O.D. test (biochemical oxygen demand) measures the biodegradable organic matter in water. It is a test - like the weather - which everyone criticizes but no one does much about it. The test is time-consuming since it requires a five-day incubation period, but so far it is the best measuring stick we have.

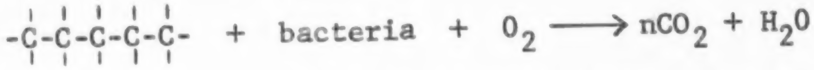
Historically, it is believed that the B.O.D test began in London, England toward the turn of the century. It was estimated that domestic sewage dumped into the Thames River rode the ocean tides for five days before finally reaching the open sea. Whether this be true, many scientific studies have since shown that it does take bacteria about five days to act upon domestic wastewater under optimum laboratory conditions.

Before getting down to technical and analytical details, it should be pointed out that the B.O.D test attempts to do in the laboratory what nature does in open bodies of water to remove contaminating organic matter from its streams, lakes, rivers, etc. Obviously, no laboratory procedure can duplicate this. Just what does nature do?

When natural waters are contaminated with diodegradable organic matter (animal waste; human waste; run-offs from fields, forests, swamps, wet-lands, etc.) nature initiates an immediate clean-up by calling upon ever-present bacteria to do their part in completing the carbon cycle. Bacteria, like other living organisms, need two things to live: food and oxygen. Their food is the organic waste in the water; their oxygen comes from the small amount of air which is soluble in water:

1/2 O_2	Temp.
14 ppm	0°C
11	10
8	21
7	32

The end product of the bacteria's metabolism is CO_2 - and their dead bodies. Schematically, the reaction may be over-simplified as:



$$-C-C-C-C-C- + \text{bacteria} + O_2 \longrightarrow nCO_2 + H_2O$$

Up to a point, the above natural process efficiently and effectively kept our waters clean and productive. But even the heroic - if futile - efforts of Mother Nature has been unable to cope with the excessive burden of waste - domestic and industrial - which our exploding civilization dumps into many of the nation's major and minor bodies of water. Fortunately - or unfortunately - in badly polluted water, the above reaction depletes all the dissolved oxygen in the water, so thatnone - or too little -

remains for the sustenance of marine life. The break point is about 3.5 ppm of dissolved oxygen (D.O.) and severely polluted water often contains less than 1.0 ppm of D.O. - thus fish and other aquatic life cannot survive.

First, let's describe the B.O.D. test in lay language. A quantity of water under test is taken which contains sufficient organic contaminants to about half deplete the dissolved oxygen contained in a total volume of 300 ml of water; that is, the sample plus an added amount of water to fill a 300 ml of B.O.D. bottle. The "added water" is referred to as dilution water; it contains dissolved oxygen, bacteria, and nutrients to feed the bacteria. The D.O. contained initially in the 300 ml bottle is then determined; this is compared to the D.O. remaining after incubation at 21°C. for 5 days. (The D.O. is lowered during incubation due to the bacteria consuming the organic contamination in the water, and in so doing using up part of the dissolved oxygen.) The difference in D.O. - before and after incubation - divided by the amount of sample used, is the B.O.D.; it measures the organic matter in water that is susceptible in bacterial action.

Exercise 2

What is meant by D.O.?

Exercise 3

Why is a 5-day incubation period used in this test?

Exercise 4

Why is 21°C used as the incubation temperature?

Exercise 5

What are we measuring in a B.O.D. test?

At the risk of insulting your intelligence, the importance of thoroughly cleaning the B.O.D bottles should be emphasized. Don't use acid-dichromate since this might leave a residue that would be toxic to bacteria. Ordinary soap or detergent may be used followed by several minutes of rinsing with running tap water. It is possible to make a rinsing apparatus by taking six 1/8" copper tubes and soldering them into a manifold over which the bottles are placed upside down. After the rinse, each bottle is rinsed with distilled water.

The sample is then added to the 300 ml B.O.D. bottle. The amount of sample is largely governed by experience. For domestic sewage about 3 ml is a good guess; if the water sample is particularly clean, as much as 250 ml may be used. The reasoning behind this will be more apparent after you have completed some sample calculations. In almost all cases, three dilutions are used: one above and one below the level you guess - from experience - to be about right.

THE DILUTION WATER

Unless unusual conditions are encountered (in which case be guided by Standard Methods) the dilution water is made by adding 20 ml each of the following to 5 gallons of distilled water:

(1) Phosphate buffer	8.5g. KH_2PO_4	
	21.75 K_2HPO_4	Make to 1 liter
	33.4 $Na_2HPO_4.7H_2O$	pH = 7.2
	1.7 NH_4Cl	
(2) $MgSO_4$	22.5g. $MgSO_4.7H_2O$ per liter	
(3) $CaCl_2$	27.5g. $CaCl_2$ per liter	
(4) $FeCl_3$	.25g. $FeCl_3.6H_2O$ per liter	
* (5) $Na_2S_2O_3$	1.575g. $Na_2S_2O_3$g/1	Prepare daily.
(6) Seed	domestic sewage stored for 24 hours	

Saturate with oxygen by bubbling air thru the solution over-night using a fritted foot.

After adding the samples to the B.O.D. bottles, fill them with the dilution water and shake. As noted above, duplicates are prepared: one is analyzed immediately for dissolved oxygen, and the other is incubated for 5 days at 21°C.

To determine the dissolved oxygen in aqueous solutions, the following reagents must be prepared. Use automatic pipettes, if available, for measuring out and adding the 2 ml portions noted below.

REAGENTS FOR DETERMINING D.O.

(a) $MnSO_4$ 480g/1 of $MnSO_4.4H_2O$ (filter)

(b) Alkali-iodide-azide solution

Dissolve 500g of NaOH in 500 ml of boiled and cooled distilled water.

Then add 150g. of NaI to the caustic solution.

---

* Add the $Na_2S_2O_3$ if residual chlorine is present. (See Standard Methods.)

Dissolve 10g. of NaN_3 in 400 ml of distilled water and add to the above. Make up to 1 liter.

(c) $\underline{H_2SO_4}$ Add 22g. of Ag_2SO_4 to a 9 lb. bottle of H_2SO_4

(d) $\underline{N/40\ Na_2S_2O_3.5H_2O}$ Dissolve 6.5g. in 1 liter of distilled water.

(e) $\underline{N/40\ K_2Cr_7O}$ Dissolve 1.2258g. in 1 liter of distilled water.

PROCEDURE

The procedure and the chemistry involved in analyzing for dissolved oxygen in water is as follows:

(a) Add 2 ml of the $MnSO_4$ to a full 300 ml B.O.D. bottle.

(b) Immediately thereafter, add 2 ml of the alkali-iodide-azide solution, stopper the bottle tightly and shake; a precipitate forms. If no D.O. is present, there is no change in the oxidation number of the Mn.

(c) Allow the precipitate to settle, add 2 ml of the H_2SO_4, shake the bottle thoroughly and allow to stand for a few minutes. I_2 is released in this reaction.

(d) Using a 250 ml graduated cylinder, measure 204 of the above solution into a wide-mouth Erlenmeyer flask (a magnetic stirrer is helpful) and titrate the I_2 with the N/40 $Na_2S_2O_3$ solution, using starch towards the end-point as the indicator. The $Na_2S_2O_3$ is oxidized to $Na_2S_4O_6$.

Exercise 6

What is the balanced equation for the reaction between $MnSO_4$ and NaOH?

If D.O. is present the oxidation number of Mn goes from 2+ to 4+.

Exercise 7

What is the balanced equation for the reaction between $MnSO_4 + NaOH + O_2$?

Exercise 8

What is the balanced equation for the reaction between MnO_2, KI and H_2SO_4?

Exercise 9

What is the balanced equation for the reaction between $Na_2S_2O_3$ and I_2?

If the $Na_2S_2O_3$ is exactly N/40, each ml used in this step is equivalent to 1 ppm of D.O. Here's why:

Checking the above three oxidation-reduction reactions in steps (b), (c), and (d) you will find that two electrons are involved in each reaction. Thus one mole of $Na_2S_2O_3$ is equivalent to one mole of D.O. Dissolved oxygen (0) - that is 1/2 O_2 - has a valence of -2 and an atomic weight of 16. Thus it has an equivalent weight of 8. Therefore:

$Na_2S_2O_3$		D.O.
1 liter of 1 N solution	=	8 g/1
1 liter of 1/8 N solution	=	1 g/1
1 liter of 1/40 N solution	=	1 g/200ml (Divide each side by 5)
1 ml of 1/40 N solution	=	0.001 g/200ml

So it is that 200 ml (204 ml allows for loss due to the addition of reagents) is used in the above step 4.

Actually, it is impractical to prepare a $Na_2S_2O_3$ solution which is exactly N/40. Furthermore, the solution changes strength on standing and must be standardized every day it is used. Thus N/40 N solution of $K_2Cr_2O_7$ is used for standardization since it is quite stable and can be prepared accurately. Two steps and two oxidation-reduction reactions are involved:

In the first reaction $K_2Cr_2O_7$ reacts with KI and H_2SO_4 to produce Cr^{3+}, free iodine, water and a salt.

Exercise 10

What is the balanced equation for the reaction between $K_2Cr_2O_7$ KI and H_2SO_4?

The I_2 formed in this reaction then reacts with $Na_2S_2O_3$ just as it did in Exercise #9.

Exercise 11

What is the balanced equation for the reaction between $Na_2S_2O_3$ and I_2?

In Exercise #10 above, the two Cr's in $K_2Cr_2O_7$ and in $Cr_2(SO_4)_3$ change their oxidation numbers.

Exercise 12

What is the total oxidation number of the two Cr's in $K_2Cr_2O_7$?

Exercise 13

What is the total oxidation number of the two Cr's in $Cr_2(SO_4)_3$?

Exercise 14

What is the total difference in oxidation numbers?

Since the total difference is 6 we would have to do the following in order to make a N/40 solution:

$K_2Cr_2O_7$(m.w. = 294.2)

g/l		Strength
294.2	=	6 N
294.2/6 = 49.03	=	1 N
49.03/40 = 1.2258	=	N/40

The student should note in the above two equations that there is a one-to-one electron relationship between the N/40 $K_2Cr_2O_7$ and the N/40 $Na_2S_2O_3$. Actually that is what normality means in oxidation-reduction reactions: the gain or loss of one electron. In practice, then, the strength of the $Na_2S_2O_3$ is determined by titrating it against the standard $K_2Cr_2O_7$ and the $Na_2S_2O_3$ readings corrected accordingly.

At long last, we are prepared to define what is meant by B.O.D. It is the dissolved oxygen - D.O. - in parts-per-million (ppm) required to react with 1g. of biodegradable organic matter. Thus, if sewage has a B.O.D. of 300, this means that it takes 300ppm of D.O. to react with 1g. of the sewage.

Let us assume that we have 1g. of such sewage.

Exercise 15

How many ppm of D.O. does 1g. of sewage equal?

Exercise 16

How many grams of D.O. per gram of water is 300 ppm equal to?

Exercise 17

How many grams of D.O. is needed to react with 1 lb. of this sewage? (1 lb. = 454 g.)

Exercise 18

How many grams of D.O. are needed to react with 1 gal. of sewage? (1 gal. = 3780 g.)

Exercise 19

How many gallons of water, whose D.O. = 8 ppm, would be needed to "cleanse" one gallon of sewage and still leave 4 ppm of D.O. in the streams to support marine life?

DETERMINATION OF B.O.D.

To determine the B.O.D. of a water sample, the following analyses are made:

$D.O._s$	Dissolved oxygen in original sample.
$D.O._b$	Dissolved oxygen in blank (dilution water only) after incubation.
$D.O._i$	Dissolved oxygen in sample plus dilution water after incubation. (add sample to 300ml B.O.D. bottle and fill it with dilution water and incubate.) As noted above, two additional samples are taken, one above and one below the level thought to be about right.

Procedure

(1) Add 2ml of $MnSO_4$, plus 2ml of alkali-iodide-azide solution. Stopper, shake well, let precipitate settle.

(2) Add 2ml of H_2SO_4, stopper, shake well.

(3) Titrate 204ml of the solution with N/40 $Na_2S_2O_3$, which has been standardized against N/40 $K_2Cr_2O_7$. The

corrected burette reading of the N/40 $Na_2S_2O_3$ is the D.O.

Calculation

The calculation of B.O.D. can be best understood by following an actual analysis. For example, a 4ml sample of waste water was analyzed and the following data obtained:

$D.O._s = 0.2$ ppm

$D.O._b = 7.5$ ppm

$D.O._i = 3.5$ ppm

Obviously, the dissolved oxygen initially available to the bacteria in the B.O.D. bottle is the total of that contained in the sample plus that contained in the dilution water.

Exercise 20

What is the volume of dilution water?

Exercise 21

What is the volume of sewage sample?

Exercise 22

What is the dissolved oxygen available in the dilution water?

Exercise 23

What is the dissolved oxygen available in the sewage sample?

We must now subtract the dissolved oxygen in the 300ml bottle after incubation.

Exercise 24

What is the value?

The oxygen used by the bacteria to "eat" the organic matter in the waste water is therefore:

$[(300-4)x7.5 + 4x0.02] - [300x3.5]$ for a 4ml sample.

One-fourth of this for a 1ml sample: upon rearrangement we therefore have

$$\frac{300(7.5 - 3.5)}{4} - (7.5 - 0.2) = 300.$$ This is the B.O.D. ignoring the 7.3.

The general formula is obvious from the above:

$$B.O.D. = \frac{\text{Volume of bottle}}{\text{ml of sample}} \left[(D.O._b - D.O._i)\right] - (D.O._b - D.O._s)$$

The $(D.O._b - D.O._s)$ is ignored if it is less than the limit of error of the test data.

The B.O.D. is reported as the average of the three samples analyzed. However, the differences between the $(D.O._b - D.O._i)$ must be significant in order to give a meaningful result. If all the dissolved oxygen is used - or very little - then the data for that analysis has little or no value.

Now you calculate the B.O.D of the following three samples of water:

Exercise 25		Sample Size	$D.O._b$	$D.O._i$	$D.O._s$
	I	2 ml	7.2	6.4	0.5
		4	7.1	5.1	0.5
		6	7.0	4.0	0.5
Exercise 26					
	II	50	7.5	5.5	7.0
		100	7.6	3.3	7.0
		200	7.8	0.6	7.0
Exercise 27					
	III	10	7.8	5.1	3.3
		15	7.6	3.5	3.3
		20	7.6	1.9	3.3

C.O.D.

The Chemical Oxygen Demand (C.O.D.) test is used for two reasons:

(1) It takes several hours rather than 5 days.

(2) It reacts with many organic pollutants that are not affected by bacteria.

If toxic substances are present in water that kill bacteria, this test - or a total carbon determination - may be the only method capable of measuring the organic matter present in a sample of water.

In some cases, it can be shown that the C.O.D. is related to the B.O.D. by a constant factor; C.O.D. is always higher than B.O.D. If nothing happens in the water to change or upset this relationship, the chemist knows from repeated analyses just how much C.O.D. is equivalent to B.O.D. Thus he doesn't have to wait 5 days for his analysis. However, if something does happen to upset this relationship, then the deduction is misleading and wrong.

The C.O.D. test uses strong oxidizing agents to "chew up" the organic matter in water; thus the results of this test are always higher than the B.O.D. Actually, the reactants used - $K_2Cr_2O_7$ and H_2SO_4 - oxidize most organic compounds and many that are not biodegradable. For example, glucose and wood pulping wastes such as lignin are measured by the C.O.D. test, which the B.O.D. test won't touch. Even so, some aromatic organic molecules are not destroyed by the strong oxidants used in the C.O.D. test.

It is important to note that $K_2Cr_2O_7$ is not reduced by ammonia or the ammonia liberated from proteins.

An oversimplification of the chemical reaction which occurs during the C.O.D. test is:

$$2K_2Cr_2O_7 + 8H_2SO_4 + C_xH_yO_z \longrightarrow xCO_2 + 1/2yH_2O + 2Cr_2(SO_4)_3 + 2K_2SO_4$$

Note that is this equation there is a change of 6 electrons:

$$\overset{(2x6+)}{(Cr_2O_7)^{-2}} + 6e \longrightarrow \overset{(2x3+)}{Cr_2}$$

Solutions for C.O.D. determinations

Standard 0.25 N $K_2Cr_2O_7$ (m.w. = 294.2)

1 N solution = 294.2/6 = 49.033 g/l

0.25 N " = 49.033/4 = 12.259 g/l

0.12g of sulfamic acid are added to avoid interference by nitrates.

Concentrated H_2SO_4

Add 22g. Ag_2SO_4 to a 9 lb. bottle of concentrated H_2SO_4

Standard ferrous ammounium sulphate

Dissolve 39g. $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add

20ml of concentrated H_2SO_4 and dilute to 1 liter.

Ferroin indicator

Dissolve 1.485g. of 1,10-phenanthroline mono-hydrate plus 0.695g. $FeSO_4.7H_2O$ in water and dilute to 100ml.

Standardization

Measure 10ml of standard $K_2Cr_2O_7$ from a burette into about 100ml of distilled water. Add 30ml of concentrated H_2SO_4 and allow to cool. Titrate with ferrous ammonium sulphate using 3 drops of the ferroin indicator.

$$\text{Normality of } Fe(NH_4)_2(SO_4)_2 = \frac{\text{ml of } K_2Cr_2O_7 \times 0.25}{\text{ml of } Fe(NH_4)_2(SO_4)_2}$$

Procedure

(a) Into a 300ml refluxing flask topped with a vertical condenser put:

0.4g $HgSO_4$

20ml of sample

10ml of standard $K_2Cr_2O_7$ solution from burette

30ml of concentrated H_2SO_4 containing Ag_2SO_4

(b) Reflux at the boil for 2 hours.

(c) Cool and wash down condenser and flask.

(d) Dilute to about 150ml withdistilled water and cool.

(e) Add 3 drops of ferroin indicator.

(f) Titrate with ferrous ammonium sulphate.

End point: blue green to reddish brown.

Calculations

$$\text{C.O.D.} = \frac{(a-b) \times c \times 8000}{\text{ml of sample}} \text{, in ppm}$$

a = ml of $Fe(NH_4)_2(SO_4)_2$ used for titrating blank.
b = " " " " " " sample.
c = normality of $Fe(NH_4)_2(SO_4)_2$

As to the why of the above calculation, one liter of any reagent is equivalent to the gain or loss of one mole or electron.

Therefore:

1 liter of 1 N $K_2Cr_2O_7$ = 1 equivalent of O^{-2}

1 ml of 1 N " = .001 " " "

(An equivalent of $O^{-2} = 1/2 \times 16 = 8$g.)

1 ml of 1 N $K_2Cr_2O_7$ = 0.008g. of oxygen

$$= 8 \times 10^{-3} = \frac{8}{10^3} \times \frac{10^3}{10^3} = \frac{8000}{10^6} =$$

8000 ppm.

ANSWERS

A. Pretest

1. $\text{waste} + O_2 \xrightarrow{\text{bacteria}} CO_2 + H_2O$

   $CO_2 + H_2O \xrightarrow{\text{photosynthesis}} \text{plants}$

   Plants are digested and some discharged as wastes, which then can recycle.
2. (2)
3. (1)
4. (1)
5. (1)
6. $2C_6H_{14} + 19O_2 \rightarrow 12O_2 + 14H_2O$
7. $3C_{11}H_{22}O_{11} + 22K_2Cr_2O_7 + 88H_2SO_4 \longrightarrow 33CO_2 + 121H_2O + 22K_2SO_4 + 22Cr_2(SO_4)_3$
8. $\frac{\text{m.wt.}}{6} = 49.03$ g/Eq.
9. 76 ppm.
10. 48 ppm.

ANSWERS

B. Study Guide

Exercise 1

This answer is discussed in the following paragraph of this text.

Exercise 2

Dissolved oxygen is the amount of oxygen dissolved in the water sample expressed as ppm.

Exercise 3

The change in D.O. levels out after 5 days of incubation.

Exercise 4

Experience has shown that 21°C is about optimum for promoting the growth of bacteria most effective for feeding upon domestic wastes.

Exercise 5

We are measuring the difference in dissolved oxygen levels, due to bacterial growth converting organic matter into CO_2.

Exercise 6

$$MnSO_4 + 2NaOH \longrightarrow Na_2SO_4 + Mn(OH)_2$$

Exercise 7

$$MnSO_4 + 2NaOH + O_2 \longrightarrow MnO_2 + H_2O + Na_2SO_4$$

Exercise 8

$$MnO_2 + KI + 2H_2SO_4 \longrightarrow MnSO_4 + I_2 + 2H_2O + K_2SO_4$$

Exercise 9

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

Exercise 10

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3I_2 + 7H_2O + 4K_2SO_4$$

Exercise 11

Same as #9.

Exercise 12

Total oxidation number = 12.

Exercise 13

Total oxidation number = 6.

Exercise 14

Total difference = 6.

Exercise 15

300 ppm (information given above).

Exercise 16

$300g/10^6g = 3 \times 10^{-4}g$. D.O./g.$H_2O$ to react with 1 g. of sewage.

Exercise 17

3×10^{-4} g. D.O./g. sewage x 454 g. sewage = 0.136 g. D.O. (1 lb. = 454 g.)

Exercise 18

1 gal. sewage x 3780 g. sewage/gal. sewage x 3×10^{-4} g. D.O./g. sewage = 1.13 g. D.O.

Exercise 19

If we assume water in a clean stream contains 8 ppm of D.O. and the level should not fall below 4 ppm, there is a difference of 4 ppm of D.O. for cleansing purposes. The sewage has a B.O.D. of 300.

Sewage	D.O. demand
1g.	300 ppm = 3×10^{-4} g. required per g. sewage
454 g. (1 lb.)	$454 \times 3 \times 10^{-4}$ = .136g. " " lb. "
1 gal. (8.34 lb.)	.136 x 8.34 = 1.13 g. " " gal. "

Based on the above assumptions, 4 ppm of D.O. from the clean stream are to be used to react biologically with the organic matter in the sewage. (Actually, parts-per-million can be: grams per million grams, or pounds per million pounds; it must be that the units are alike.)

The question then is: how many pounds of water containing 4×10^{-6} lbs. of D.O. are required to provide 1.13 lbs of D.O. The answer is:

$$\frac{1.13}{4 \times 10^{-6}} = 0.3 \times 10^{6} \text{ lb. of stream water}$$

$$\frac{0.3 \times 10^{-6}}{8.34} = 36{,}00 \text{ gal. of stream water}$$

Exercise 20

300 ml. - 4 ml = 296 ml.

Exercise 21

4 ml.

Exercise 22

296 ml (7.5 ppm) = 2220 ppm

Exercise 23

4 ml (0.2 ppm) = 0.8 ppm

Exercise 24

300ml (3.5 ppm) = 1050 ppm

Exercise 25

$$\text{B.O.D.} = \frac{300}{\text{sample}} (\text{D.O.}_b - \text{D.O.}_i) - (\text{D.O.}_b - \text{D.O.}_s)$$

$$\text{B.O.D.} = \frac{300}{2}(7.2 - 6.4) - (6.4 - 0.5) = 115 \text{ ppm}$$

$$\text{B.O.D.} = \frac{300}{4}(7.1 - 5.1) - (7.1 - 0.5) = 144 \text{ ppm}$$

$$\text{B.O.D.} = \frac{300}{6}(7.0 - 4.0) - (7.0 - 0.5) = 142 \text{ ppm}$$

The above should be reported as B.O.D. = 140 since the values for calculating 115 are too small to be accurate.

Exercise 26

$$\text{B.O.D.} = \frac{300}{50}(7.5 - 5.5) - (7.5 - 7.0) = 12 \text{ ppm}$$

$$\text{B.O.D.} = \frac{300}{100}(7.6 - 3.3) - (7.6 - 7.0) = 13 \text{ ppm}$$

$$\text{B.O.D.} = \frac{300}{200}(7.8 - 0.6) - (7.8 - 7.0) = 10 \text{ ppm}$$

The value is doubtful but it checks the other two fairly well, so the B.O.D. = 12.

Exercise 27

$$\text{B.O.D.} = \frac{300}{10}(7.8 - 5.1) - (7.8 - 3.3) = 76 \text{ ppm}$$

$$\text{B.O.D.} = \frac{300}{15}(7.6 - 3.5) - (7.6 - 3.3) = 78 \text{ ppm}$$

$$\text{B.O.D.} = \frac{300}{20}(7.6 - 1.9) - (7.6 - 3.3) = 82 \text{ ppm}$$

Average of the above, B.O.D. = 79 ppm

THE NITROGEN CYCLE

SUMMARY

This mini-course briefly introduces the nature of amines and amino acids and relates these to waste products, such as urea. The nitrogen cycle is described, and methods for analysis of ammonia-N, Kjeldahl-N, nitrates and nitrites are given.

RATIONALE

Nitrogen is one of the most abundant elements on this planet. It is not surprising, then, that it plays a very important role in every form of life - human, animal, vegetable and aquatic. Nitrogen-containing compounds are among our essential foods; they are also part of our waste products. The analysis of water for these compounds tells the chemist much about the purity - or contamination - of our streams, lakes and other bodies of water.

ACKNOWLEDGEMENT

The author is indebted to Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College, for helping to insert and answer many of the questions contained herein.

PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. Draw correct molecular structures of simple organic compounds.

2. Determine the oxidation number of the elements in a compound when given a chemical formula, using the periodic chart.

3. Do calculations with N, number of equivalents, and volume to determine any one of these when given the other two.

4. Perform acid-base titrations and neutralization calculations.

5. Prepare solutions of appropriate concentration when given the reagents and the procedure.

6. Convert from N to ppm and vice versa.

7. Use a spectrophotometer such as the Spectronic-20.

8. Define what is meant by "aerobic" and anaerobic" bacteria.

9. Use a pH meter to determine the pH of a solution to ±0.05 pH unit.

OBJECTIVES

At the completion of this mini-course, the student should be able to:

1. Give a brief description of animal and human metabolism.

2. Describe the nitrogen cycle, and specify the oxidation numbers of nitrogen in each step.

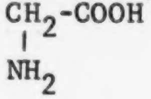
3. Analyze water samples for (a) ammonia - N
   (b) Kjeldahl - N
   (c) nitrates
   (d) nitrites

4. Discuss the analysis in objective #3. The discussion should include chemical equations as well as advantages and limitations of the procedure.
5. Define:
    - amine
    - amino acid
    - protein
    - hydrolysis
    - primary amine
    - secondary amine
    - tertiary amine
    - peptide bond
6. Identify or draw from memory the molecular structure of urea.

PRETEST

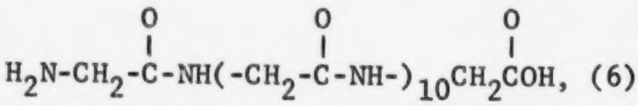
As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. Which of the following is a protein? (1) CH_3CH_2COOH, (2) $CH_3CH_2NHCH_3$, (3) $CH_3CH_2NH_2$, (4)



$\underset{\substack{| \\ NH_2}}{CH_2}\text{-}COOH$

(5)



$H_2N\text{-}CH_2\text{-}\overset{\substack{O \\ |}}{C}\text{-}NH(\text{-}CH_2\text{-}\overset{\substack{O \\ |}}{C}\text{-}NH\text{-})_{10}CH_2\overset{\substack{O \\ |}}{C}OH$, (6) none of these.

2. Which of the above is an amino acid?
3. Which of the above is a secondary amine?
4. Which of the above is a tertiary amine?
5. Which of the above contains one or more peptide bonds?
6. Calculate the normality of NaOH if 32.21 ml is required to neutralize 0.442 g KHP (Equivalent weight = 204 g).
7. In a titration 25.0 ml of 0.0799N NaOH were required to neutralize exactly 20 ml of H_2SO_4. What is the normality of the acid?
8. Calculate the concentration, in ppm, of Kjeldahl-nitrogen in a sample which gave the following data: The pH of a blank distilled into boric acid was 5.2. A 200 ml sample of water, before digestion, required 8.5 ml of N/14 H_2SO_4 to return the pH to 5.2. After digestion, another 200 ml sample required 19.6 ml of the H_2SO_4 to return the pH to 5.2.
9. What is the ammonia-N in #8 in ppm?
10. What is the total-N in #8 in ppm?
11. A sample was analyzed for nitrate, giving a reading of 0.48 on the Spectronic-20. A standard solution containing 20 ppm gave a reading of 60 on the Spectronic-20 and a standard containing 10 ppm gave a reading of 0.40. What is the concentration of nitrate-N in ppm?
12. Describe the technique for Kjeldahl analysis, including advantages and limitations.
13. What is the difference in analysis for nitrates and nitrites?

I. INTRODUCTION: AMINO ACIDS AND PROTEINS

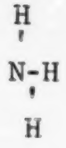
Since the earth has an abundant supply of carbon, water, oxygen and nitrogen it is not surprising that life on this planet has learned to depend upon and utilize these elements - plus many others: P, Ca, Na, K, Cl, to list but a few. Our current attention is focused on proteins, the nitrogen-containing organic compounds that are so essential to animal and human life. Proteins form one step in the nitrogen cycle.

The chemistry and physiology of nitrogen-containing compounds in warm-blooded animals is extremely complex. Perhaps of equal or greater mystery is Nature's ability to extract nitrogen from the atmosphere and incorporate it into vegetable and marine life. These actions - so basic all forms of life - are also part of the nitrogen cycle.

Exercise 1

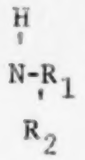
What is a protein?

At the risk of over-simplification, let us try to translate the dictionary's definition of a protein into more understandable language. Ammonia (NH_3) - like CO_2 - is one of Nature's fundamental building blocks. The "H's" in NH_3 can be replaced by organic radicals (called R-groups) to form amines:



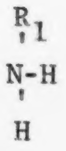
$$\begin{array}{l} H \\ | \\ N-H \\ | \\ H \end{array}$$

ammonia



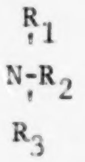
$$\begin{array}{l} H \\ | \\ N-R_1 \\ | \\ R_2 \end{array}$$

Secondary amine



$$\begin{array}{l} R_1 \\ | \\ N-H \\ | \\ H \end{array}$$

primary amine



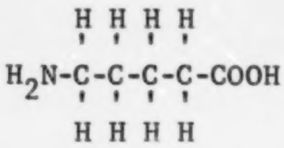
$$\begin{array}{l} R_1 \\ | \\ N-R_2 \\ | \\ R_3 \end{array}$$

tertiary amine

You will recall that an organic acid has the following structure, where R is an organic radical of almost infinite variety and complexity:

RCOOH (Note that CO_2 is central to this molecule).

It often happens that an amine and an organic acid can be combined in a single molecule. These are called amino acids; their structure can be relatively simple or quite complicated:



$$H_2N-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-COOH$$

Exercise 2

Are amines basic or acidic?

Exercise 3

In terms of being acidic or basic, what is unusual about an amino acid?

Exercise 4

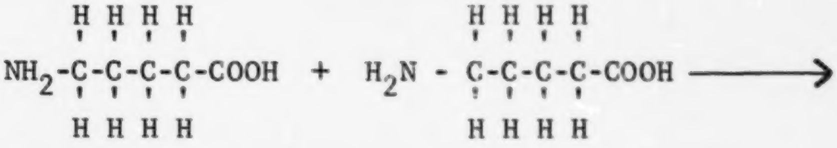
a. What products are formed when an acid reacts with a base?

b. What product would form if the acid H^+ on $H_2NCH_2CH_2CH_2CH_2COOH$ were transformed to the basic site on the same molecule?

Upon dehydration, the $-NH_2$ on one amino acid can combine with the COOH of another amino acid to form what is appropriately called an "acid-amide". The $R-\overset{\overset{O}{\|}}{C}-NH-R_1$ linkage is called a peptide bond.

Exercise 5

What would be the products to the following reactions if a water molecule is extracted from between these two amino acids?



$$NH_2-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-COOH + H_2N - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-COOH \longrightarrow$$

The acid end of the product molecule can react with the amine end of another molecule to form a still larger molecule, just as the amine end can react withanother acid end. This process can and does continue until very large and very complex molecules are formed. The complex and large molecules formed by joining together 10 more amino-acids are called proteins.

So far as our metabolism is concerned, proteins build and replenish the muscles that do our bodies' work.

Exercise 6

Where does our body get the energy for replenishing the muscles that do our work?

Exercise 7

What would you say is the cause of malnutrition suffered by many people of the world?

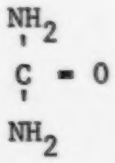
Exercise 8

From the above, what would you think is the procedure by which our digestive system breaks down food and passes off waste materials?

Exercise 9

What is the basic ingredient in urine excreted from our body?

The formula for urea is:



$$\begin{array}{c} NH_2 \\ | \\ C = O \\ | \\ NH_2 \end{array}$$

Exercise 10

What is the balanced equation for the hydrolysis of urea?

Seldom, if ever, does our digestive system utilize all the food we eat. Therefore, undigested proteins and other nitrogen-containing compounds are present in the feces. So the chemist analyzes water for ammonia and other nitrogen containing compounds, for their presence is evidence of probable pollution by human and /or animal body wastes. The situation is further complicated by the fact that nitrogen has many oxidation numbers.

II. THE NITROGEN CYCLE

A. The Chemistry of Nitrogen

Nitrogen is in the fifth group of the Periodic Table. This means that it has five electrons in its outer orbit. It can therefore lose these five electrons or gain an additional three to achieve the stable configuration of eight electrons in its outer orbit. The gain of three electrons results in a valence of -3 as in NH_3; the loss of five electrons produces N^{+5} as in HNO_3. Actually, nitrogen forms compounds in every valence state from -3 to +5, for a total of nine. Only four of these concern the water chemist.

Exercise 11

What are the oxidation numbers in the following table?

	Compound	Oxidation number
NH_3	ammonia, amines and proteins	(a) _____
N_2	atmospheric nitrogen	(b) _____
$(NO_2)^{-1}$	nitrites	(c) _____
$(NO_3)^{-1}$	nitrates	(d) _____

Organic nitrogen is defined as those organic compounds which contain nitrogen. This does not include NH_3 even though the valence of nitrogen is -3 in both ammonia and organic compounds containing nitrogen. Thus the chemist analyzes a water sample for ammonia by a good analytical procedure; then the sample is analyzed for the remaining organic nitrogen compounds using the Kjeldahl method. The sum of the ammonia-nitrogen and the Kjeldahl-nitrogen is reported as total nitrogen. More will be said about this later.

Exercise 12

What is the origin of these organic nitrogen compounds in our waste?

Exercise 13

What does nature do to try to overcome the effect of these pollutants?

Thus the chemist learns much from the ammonia and total organic nitrogen content of a water sample. The presence of such compounds strongly indicates animal and/or human waste contamination.

In the mini-course dealing with bacteriology, the role of aerobic and anerobic bacteria will be discussed in some detail.

For the present, it is assumed that the student knows that aerobic bacteria depend upon oxygen for their growth; anerobic bacteria grow is the absence of oxygen. Depending upon the condition of the water - whether dissolved oxygen is present - Nature uses both types of bacteria for coping with nitrogen-containing pollutants. Except in extremely bad situations, some dissolved oxygen is present in water and thus the aerobic bacteria predominate. They promote the following reations:

I $\quad$ Proteins + bacteria $\longrightarrow NH_3$ + other products

II $\quad 2NH_3 + 3O_2 + \text{bacteria} \longrightarrow 2HNO_2 + 2H_2O$

III $\quad 2HNO_2 + O_2 + \text{bacteria} \longrightarrow 2HNO_3$

Under anerobic conditions - which can occur in stagnant ponds, lakes and other badly polluted bodies of water - anerobic bacteria reduce nitrites to atmospheric nitrogen. This is one of the ways the nitrogen cycle is completed.

To summarize:

(1) About 80% of the world's atmosphere is N_2.

(2) Life - animal and human - on the earth depends upon nitrogen compounds, particularly proteins.

(3) Lightning produces large amounts of HNO_3 from the atmosphere which fertilizes the land and the ocean.

(4) Certain plants can "fix" nitrogen from the atmosphere.

(5) Aquatic and land plants convert nitrogen compounds into proteins.

(6) Mankind and animals need proteins for their metabolism.

(7) The waste products of men and animals are converted by bacterial action into NH_3, HNO_2, HNO_3, and N_2.

(8) These feed plant life or are returned to the atmosphere, thus completing the nitrogen cycle.

To this point, we have seen that the chemist analyzes water for B.O.D. and nitrogen-containing compounds. Both measure organic contamination, but the presence of significant amounts of ammonia, organic-nitrogen, nitrates and nitrites strongly indicate the presence of domestic or animal body waste.

Let us now see what is meant by a term used above and frequently used in water chemistry; that term is "Kjeldahl nitrogen". After removing the ammonia from a sample of water by addition of strong base and heating, the sample is digested with boiling H_2SO_4 plus a catalyst.

Exercise 14

What is the purpose of digesting the sample with sulfuric acid and the catalyst?

This destroys the organic matter in the sample and at the same time converts any organic nitrogen, such as amines and proteins - into $(NH_4)_2SO_4$. The ammonia in this compound is then released by addition of base and measured quantitatively; this is Kjeldahl nitrogen. Ammonia plus Kjeldahl nitrogen is reported as total organic nitrogen.

Many water samples are not analyzed for nitrites and nitrates because they are usually present in such small amounts. In special cases, however, these are important tests that the chemist must be prepared to make. They are also some what involved and difficult.

The interpretation of data is as important as getting accurate analysis in the first place. The proper interpretation of ammonia, Kjeldahl-nitrogen, nitrites and nitrates often requires considerable experience and supporting information on the part of the chemist. For example, the results of an analysis of a sewage plant's effluent is one thing; the analysis of the water intake of a purification plant is quite a different matter. Later study guides will discuss these matters in some detail. For the present, let us assume the role of the chemist in a water purification plant. He would suspect pollution due to domestic or animal wastes if the raw water entering the plant exceeded the following values:

Analysis	N (expressed in ppm)
NH_3	0.2
Kjeldahl nitrogen	2.0
Nitrites	0.03
Nitrates	5.0

Standard Methods is the "bible" for all water analyses, but the procedures are often difficult to follow because of cross references between various parts of the book. The following summary should therefore be helpful, but Standard Methods should be used if unusual conditions are encountered. In general, ammonia and Kjeldahl-nitrogen can be determined by (a) titration and/or (b) Nesslerization. The former is usually preferred and is given below; Nesslerization is used if the levels are quite low.

The laboratory equipment used is usually a Kjeldahl still and digestion unit, both of which are listed is scientific equipment catalogs. If the work load does not justify such an investment, ordinary glass condensers and heating units can be used; a fume hood is almost essential.

III. DETERMINATION OF AMMONIA AND KJELDAHL-NITROGEN

A. Preparation of Solutions

0.5 M phosphate buffer

Dissolve 14.3g. KH_2PO_4] in 1 liter of distilled water
68.8g. K_2HPO_4]

Standard H_2SO_4

Dissolve 2ml of concentrated H_2SO_4 in 1 liter of distilled water.

This gives N/14 H_2SO_4, so that 1 ml = 1 mg. of N

The N/14 H_2SO_4 must be standardized against N/14 NaOH, which in turn is standardized against an accurately weighed amount of potassium acid phthalate.

Boric Acid

Dissolve 20g. boric acid (H_3BO_3) in 1 liter of distilled water.

This solution must be made fresh every 30 days.

(Standard Methods adds an indicator to determine the end point but a pH meter is better and its use is described below.)

NaOH + $Na_2S_2O_3$ solution

Dissolve 500g. of NaOH and 25g. of $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

Digestion reagent

Dissolve 134g. of K_2SO_4 in 650ml of distilled water plus 200ml of concentrated H_2SO_4.

Add with stirring, a solution of 2g. of HgO in 25ml of 6 N H_2SO_4. Dilute the combined solutions to 1 liter with distilled water.

B. Procedure for Determining Ammonia-N

(1) Steam out still. Put about 400ml of distilled water into a 500ml Kjeldahl flask and distill over 200ml.

(2) Put 250ml of sample into a 500ml beaker, neutralize to pH = 7.0 using pH meter. A magnetic stirrer is helpful.

(3) Add 40ml of buffer solution, adjust to pH = 7.4 with NaOH.

(4) Pour above into a 500ml Kjeldahl flask and dilute to 400ml with distilled water.

(5) Using a distillation set-up, distill about 200ml into a wide-mouth Erlenmeyer flask containing 50ml of boric acid.

(6) Run a blank. Repeat steps (3), (4), and (5) above using distilled water instead of a sample of water.

(7) Determine the pH of the blank, after distillation into the 50ml of boric acid.

(8) Take the distilled sample - step (5) above - and titrate with N/14 H_2SO_4 until the pH is the same as the blank in step (7) above.

Calculation

$$\text{mg/l of N-ammonia} = \frac{\text{ml of N/14 } H_2SO_4 \times 1000}{\text{ml of sample}}$$

Standardizing the H_2SO_4

First prepare N/14 NaOH by dissolving about 3g. of NaOH in a liter of distilled water.

Standardize the N/14 NaOH by weighing out potassium acid phthalate - using an analytical balance.

About 0.7000g. of KHP should give a titration of 40+ ml. Titrate the NaOH against the H_2SO_4 and determine the exact normality of the H_2SO_4 accordingly.

Exercise 15

(a) What is the normality of a NaOH solution if it takes 42.7ml to neutralize 0.6860g. KHP (equivalent weight of KHP = 204g.)?

(b) It took 33.4ml of the above NaOH to neutralize 40ml of a solution of H_2SO_4. What is its normality?

Exercise 16

What is the concentration, in ppm, of N in the following solution? The pH of the blank distilled into boric acid solution was 5.4. A 250ml sample of water distilled into boric acid solution had a pH = 6.9. It took 6.6ml of the above H_2SO_4 to reduce the pH to 5.4.

Exercise 17

What is the N concentration, in ppm, if after a Kjeldahl distillation of the sample remaining in #16, it was found that it took 18.3 ml of the H_2SO_4 solution from Exercise 15(b) to titrate the boric acid solution back to its original pH?

Exercise 18

Based on the answers to questions #16 and #17, what is the concentration of total nitrogen?

IV. DETERMINATION OF NITRATES

A. Preparation of Solutions

Buffer solution

Dissolve 34g. of sodium acetate ($NaC_2H_3O_2.H_2O$) in 1 liter of distilled water. Filter the solution.

Add 100ml of dilute HCl (1ml of concentrated HCl + 99ml of distilled water) to 1 liter of the sodium acetate solution.

Sulfanilic acid

Dissolve 3.0g. of sulfanilic acid in 350ml of hot distilled water; cool. Then add 100ml of concentrated HCl and dilute to 500ml. Mix well.

Naphthylamine hydrochloride

Dissolve 3 0g. of 1-naphthylamie hydrochloride in a solution containing 150ml of distilled water, 5ml of concentrated HCl and 250ml of 95% ethyl alcohol.

Dilute to 500ml with distilled water. Mix well.

Just before using this solution, mix some of it with activated charcoal and double filter - that is, filter twice.

Color reagent

Mix equal amounts of the above sulfanilic acid and naphthylamine hydrochloride solutions the day that tests are made. Protect from light by keeping in a cabinet when not in use.

Zinc metal

This should be 20-30 mesh granular Zn. Wash with $CHCl_3$ before using to remove any oil that may be present.

Stock nitrate

Dissolve 7.2180g. of anhydrous KNO_3 in 1 liter of distilled water. This is a nitrate concentration equivalent to 1000 ppm of N.

Standard dilutions

Using the above stock solution:

1/100 = 10 ppm of NO_3^{-1}, calculated as N

Using the 10 ppm solution:

10/100 = 1 ppm of NO_3^{-1}, calculated as N

50/100 = 5 ppm of NO_3^{-1}, calculated as N

B. Procedure for Determining Nitrates

This procedure depends upon the development of color due to the reaction of nitrites with the color reagent. When available, a visible spectrometer - such as the Spectronic 20 - is recommended. It is set to absorb at 520mu. Otherwise a colorimeter is used, and the intensity of the color developed by the sample is compared to that of standards of known nitrate content.

Note in the above that the color developed is due to nitrites even though the test is for nitrates. The purpose of the granular zinc is to reduce the nitrates to nitrites. For determining nitrites, no zinc is used.

The following procedure assumes the use of a Spectronic 20:

(1) Introduce 20ml of sample, standard, or blank into a clean 250ml Erlenmeyer flask.

(2) Add 2.5ml of buffer solution and mix well.

(3) Add 5g. of Zn and shake for 4 minutes in a laboratory shaker. Filter to remove the Zn; do not wash or dilute.

(4) Add 5ml of color reagent, and let develop for 1 minute.

(5) Add 2.5ml of buffer solution, mix well, and let color develop for 5 minutes in a 60°C. constant temperature bath. Quickly rinse a test tube cell with the sample, fill the cell, insert in the Spectronic 20 and read at 520mu.

IMPORTANT: In using the Spectronic 20, it is important to have readings less than 0.75 and greater than 0.25 transmittance. Within these values, a straight line relationship holds fairly well. That is, Beer's Law applies.

If the readings fall outside these limits, other concentrations should be used so that the values are within these limits.

C. Calculations

The values obtained for the standards are plotted, a straight line is drawn between the points, and the reading for the sample located on this plot. This is then multiplied by the dilution factor.

For example, the following readings were taken:

5ppm standard = 0.173; 10ppm standard = 0.222

Sample diluted 20/1 = 0.251; this equals 13 ppm from plot. Thus 20 x 13 = 260ppm nitrate in sample, calculated as N.

D. Correction for Nitrates

It is obvious that this procedure included both the nitrate and the nitrite. The latter is usually so low by comparison that it can be ignored

Exercise 19

Starting with a NO_3^- solution containing 1000 ppm N, how would you prepare?

(a) a 100 ppm N solution

(b) a 5 ppm N solution

(c) a 4 ppm N solution

Exercise 20

A 5 ppm solution produces the following reading on a Spectronic 20 - 0.15.

A 4 ppm solution produces a 0.13 reading.

An unknown solution diluted 100 to 1 produces a 0.08 reading.

(a) What is the concentration of N in the unknown?

(b) What error in technique has been made in this experiment?

V. PROCEDURE FOR DETERMINING NITRITES

Use the same procedure as for nitrates, except:

(a) Don't use zinc.

(b) use nitrite standards of smaller concentrations, such as 0.25 and 0.50 ppm of NO_3^{-1}.

ANSWERS

A. Pretest

1. (5)
2. (4)
3. (2)
4. (6)
5. (5)
6. 0.0673N
7. 0.0999N
8. 56 ppm
9. 43 ppm
10. 99 ppm
11. 14 ppm nitrate-N

12 and 13. - See text of Study Guide

B. Study Guide

Exercise 1

The dictionary defines proteins as "any of a group of nitrogenous organic compounds of high molecular weight that contain amino acids as their basic structural units and are essential for the growth and repair of animal tissue." Dr. Lunus Pauling received the Nobel Prize in chemistry (1954) for showing that protein molecules have a helical structure of peptide chains.

Exercise 2

Amines - like their cousin ammonia - are basic.

Exercise 3

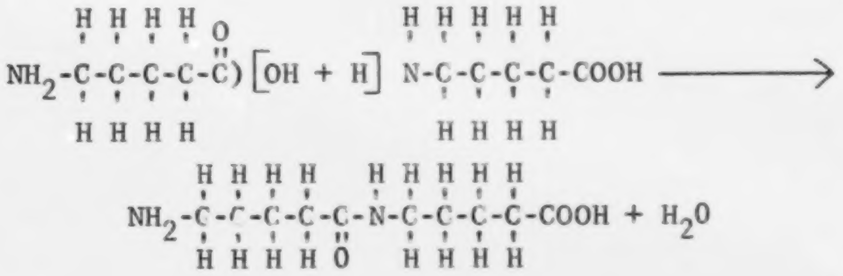
One end of an amino-acid is basic while the other end is acidic.

Exercise 4

(a) Acids react with bases to form salts, so

(b) The acid end of an amino-acid can react with the basic end of the same amino-acid to form an "internal salt" which is called a "Zwitter ion." For example, $H_3^{\oplus}NCH_2CH_2CH_2CH_2COO^{\ominus}$.

Exercise 5



$$NH_2-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}})\boxed{OH + H}\overset{H}{N}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-COOH \longrightarrow$$

$$NH_2-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{\overset{\|}{O}}{C}-\overset{H}{N}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-COOH + H_2O$$

Exercise 6

Carbohydrates supply the energy needed.

Exercise 7

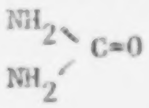
The malnutrition suffered by many people of the world is often due to an inadequate diet of well-balanced proteins - such as meat, fish, eggs, and milk.

Exercise 8

Our digestive system breaks down the food we eat - proteins, carbohydrates, etc. - by hydrolysis and other reactions - until the molecules are small enough to pass through the walls of our intestines, be absorbed by the blood stream, and transported to the various parts of the body. The waste products are returned by the blood stream, removed, and excreted as urine. The characteristic odor of urine indicates that it contains ammonia and related compounds. These are the by-products of the proteins that we ate a day or so ago.

Exercise 9

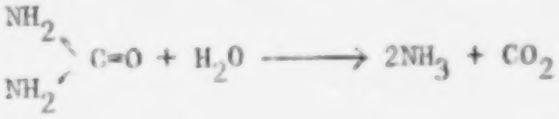
In addition to small amounts of ammonia, urine contains urea:



$$(NH_2)_2C{=}O$$

Exercise 10

Urea hydrolyzes to produce more ammonia:



$$(NH_2)_2C{=}O + H_2O \longrightarrow 2NH_3 + CO_2$$

Exercise 11

(a) -3

(b) 0

(c) +3

(d) +5

Exercise 12

Effluents from a sewage disposal plant, run-off from farms, overflow of septic tanks - to mention but a few - contain large amounts of total organic nitrogen.

Exercise 13

Mixed with streams, rivers, and lakes, nature strives to destroy such pollutants by bacterial action. However, assuming that "mama knows best", Mother Nature has adjusted this biological reaction secondary to the oxidation of carbon compounds to CO_2. In other words, the bacteria that feed upon carboneous pollutants preferentially utilize the dissolved oxygen in water for their growth and reaction. If and when they have nearly completed their task, any remaining dissolved oxygen in the water is available to those bacteria whose job it is to act upon the protein-like pollutants.

Exercise 14

The digestion destroys the organic matter and converts any nitrogen into $(NH_4)_2SO_4$, thereby preventing the loss of NH_3 as a gas.

Exercise 15

(a) Since 42.7ml NaOH =O= 0.6860g KHP

$$1000 \times \frac{0.6860}{42.7} = 16.1\text{g KHP} =\!O\!= 1 \text{ liter of NaOH}$$

The equivalent weight of KHP = 204, which means that a 1 N solution contains 204g./liter.

Therefore, $\frac{16.1}{204}$ = .0789 N of the NaOH

(b) The N_2SO_4 is weaker than the NaOH because it took more of it.

$$0789 \times \frac{33.4}{40.0} = .0659 \text{ N. of } H_2SO_4$$

Exercise 16

N/14 H_2SO_4 = 0715 N

The above H_2SO_4 solution is thus weaker than N/14. Therefore it took more than it should.

$$\frac{.0659}{.0715} \times 6.6 = 6.1\text{ml of N/14 } H_2SO_4$$

$$\text{mg/l} = \text{ppm} = \frac{6.1 \times 1000}{250} = 24.4 \text{ ppm } NH_3 \text{ (as N)}$$

Exercise 17

$$\frac{0659}{.0715} \times 18.3 = 16.9\text{ml of N/14 } H_2SO_4$$

$$\text{mg/l} = \text{ppm} = \frac{16.9 \times 1000}{250} = 67.6 \text{ ppm Kjeldahl-N (as N)}$$

Exercise 18

24.4 + 67.6 = 92.0 ppm total N (as N)

Exercise 19

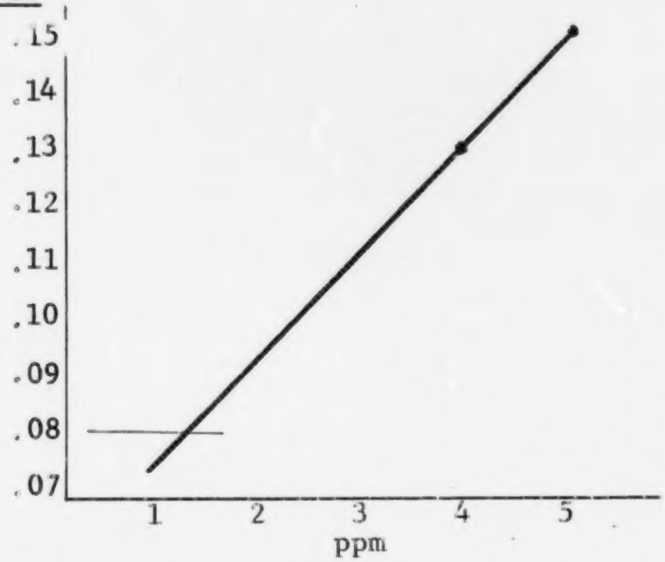
(a) 10ml of stock solution diluted to 100ml.

(b) 5ml of (a) (100 ppm) diluted to 100ml.

(c) 4ml of (a) (100 ppm) diluted to 100ml.

Exercise 20

(a)



Reading of .08 = 1 ppm.

Dilution factor of 100 to 1 = 100 x 1 = 100 ppm NO_3^{-1}(as N)

(b) The error in technique is due to the reading of the unknown solution not falling between the readings of the known solutions.

THE PURIFICATION OF WATER

SUMMARY

This mini-course summarizes the sources of potable water in the United States and describes the operation of a water purification plant. In addition, the concepts of water hardness, chlorine demand, flocculation, sand filtration, reverse osmosis, and ion exchange are covered and related to the problems of providing fresh water to the world.

RATIONALE

In large part, the United States is a great nation because it is geographically placed where there is a plentiful supply of water. Not all areas are recipients of adequate rainfall, but our vast farms and forests attest to the fact that we are indeed most fortunate.

With ever increasing demands upon our water resources - due to population growth and affluence - sufficient good water for our many needs and luxuries is becoming more and more of a major problem. The pollution of many of our natural water supplies, such as rivers, streams, and lakes, makes the task of the water chemist even more difficult.

ACKNOWLEDGEMENTS

The author is indebted to Mr. Hugo Victoreen, chief chemist of Wilmington, Delaware's Water Department, for his valuable advice and time in reviewing this mini-course. Thanks also due to Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College for inserting and answering many of the questions contained herein.

PREREQUISITES

Before beginning this mini-course, the student should be able to:

1. Use solubility equilibrium constants to calculate the solubility in M and ppm of a slightly soluble compound, and vice versa.

2. Define. amperometric titration.

3. Interconvert between M, g/l, and ppm when given the weight and molecular weight of a solute and the volume of a solution, or when given data from which these values can be calculated.

OBJECTIVES

At the completion of this mini-course, the student should be able to:

1. In terms of water availability, describe why the U.S. is one of the richest countries in the world, and discuss some limitations to the use of that water supply.

2. State three general situations an area can face with regard to the quality of its water supply.

3. State from memory at least three ions which commonly cause "hard" water.

4. Define chlorine demand, and compare the use of Cl_2 and $KMnO_4$ as oxidizing agents in water purification. Include a statement of the reason for adding the oxidizing agent.

5. Draw a rough diagram of a water purification plant, label each part, and list the 7 steps involved in the plant.

6. Describe the process of "reverse osmosis". Include a statement telling why it must be used in some areas of the world.

7. Describe the process of ion-exchange using a zeolite, including equations for removing hardness and for regeneration of the zeolite. Also include a rough diagram of an ion-exchange system with labels on the appropriate portions.

8 Calculate the weight of "hardness ions" which can be removed from water with a given sample of zeolite, or the weight of NaCl required to regenerate the exchanges.

PRETEST

As a test of your knowledge before studying this mini-course, do this pretest. Record your answers on a separate 8-1/2" x 11" sheet of paper, grade it against the correct answers, and turn in the graded sheet to the instructor unsigned. We need this information to help us evaluate this mini-course as a learning tool.

1. Using potable water as a resource, describe why the U.S. is a major world power.

2. List at least 3 ways the U.S. water supply is being threatened.

3. State the three general situations faced by an area attempting to supply potable water.

4. Given the formula for three ions which cause "hardness" in water.

5. Given Ksp for $CaCO_3 = 5 \times 10^{-9}$, calculate the concentration of Ca^{++} in water saturated with limestone in M and in ppm.

6. How could you remove the Ca^{++} above from water to make it more acceptable?

7. What effects would the Ca^{++} above have if left in the water sent to your home?

8. State 3 effects of adding Cl_2 or $KMnO_4$ to water.

9. Draw a rough diagram of a water purification plant, label each part, and list the 7 steps involved in the plant.

10. a. Using Fe^{+2} as the "hardness ion", write an equation representing the ion-exchange separation using Na^+Z^- as the zeolite.

    b. Using 1 ton of Na^+Z^-, containing 2% Na^+, what weight of Fe^{+2} can be removed before the exchanger needs recharging?

    c. Using water which contains 55 ppm of Fe^{+2}, how many liters of water can be purified by one ton of this zeolite?

I THE PURIFICATION OF WATER

> "Water, water, everywhere, and all the broads did shrink,
> Water, water, everywhere, nor any drop to drink."

The lament of the Ancient Mariner is all too familiar and tragic to many peoples of the world Their lands are barren and their throats dry, even though oceans bathe their shores.

Water- good water - is basic to life, and the greater the population in a highly affluent society such as ours, the more dependent we are on this essential commodity. Lest we forget, we are one of the most fortunate nations in the world, for we do have an abundance of good water.

But good water is only part of the story. We also have rich mines, fertile fields, vast forests, and friendly shores. We have the manpower, will power, industrial power, moderate climate, and the freedom to make the most of our resources. To date, at least, we have treasured our treasures; we must now have the willingness and farsightedness to protect and preserve them. In large part, this means to protect and conserve our water resources, for without water everything else is useless

Flying from Los Angeles to New York, it will be quite apparent that fully one-fourth of the flight is over deserts and "waste" lands which probably have treasures waiting to be discovered. Even so, the United States is a great and powerful country, in large part, because so much of it is covered with hills and mountains thatprovide the sites for natural lakes and man-made reservoirs; these in turn may be the head-waters of our rivers, streams, and/or the water supply for a village or city Cities, farms, villages, and industries naturally settle and prosper where good and abundant water is available.

On the other hand, it is estimated that surface rivers and streams carry less than 5% of the nation's rainfall to the ocean; which is another way of saying that 95% of the rainfall reaches the sea by way of large and small underground rivers and streams.

Obviously, these waters - surface and underground - will be affected by the areas through which they flow Some rural communities may be located near a brook whose waters are fit to drink - as is. Many sizable towns obtain their water from deep underground pools and pump the water directly to their customers without any treatment at all Believe it or not, New York City has no water treatment plant Clean water is piped from large upstate New York reservoirs, some Cl_2 is added, and the water pumped directly to millions of customers How fortunate can you be?

On the other hand, many communities are fortunate because their drinking water has been treated Little does the customer appreciate the privilege of turning a spigot from which flows all the good, clean water he can use - and even waste. It will be a sad day if this necessity and luxury is ever denied us; it would be much worse than an energy crisis

(Parenthetically, one responsibility the scientist has often neglected is to share his specialized knowledge with his neighbors. In this respect, the water chemist has an especially important message to tell)

Exercise 1

What comments would you make to the following remarks?

(a) The United States is a land of equal distribution of water.

(b) Our mountains make a valuable contribution to our water supply.

(c) Delaware is a state without mountains and large hills, yet it does not have any apparent shortage of drinking water.

Nationally, there is quite a difference in what happens to surface and underground waters as they gravitate to the sea. An area can face one of three general situations - and many variations thereof - regarding their water supply:

(1) Pump the water "as is" - New York City is an example.

(2) Clarify the water by removing suspended solids, dissolved iron and organic pollutants. This is true of towns and cities located on streams and rivers whose waters are reasonably low is dissolved solids, but otherwise dirty with silt and other suspended solids.

(3) Remove much of the dissolved solids if they are excessive. Florida and some western communities may face such a situation.

Exercise 2

What are two inherent problems in pumping water " as is" from an underground water supply?

(a)

(b)

Exercise 3

What is the main task of the water treatment plant?

Exercise 4

Is the amount of suspended solids and organic debris in water treated by water treatment plants constant or does it vary? Explain your answer.

The third situation noted above occurs in some regions of the United States since, underlying the soil and top-soil, there are rock formations consisting of dolomitic limestone - which is $CaCO_3$ and $MgCO_3$. The water in coastal areas may contain excessive amounts of saline intrusion. In such places, the streams, rivers and wells may have as much as 1,000 ppm of these solubilized salts. In some sections of the west, the total dissolved solids in the water exceed 2,000 ppm. In contrast, most of the water sheds in the eastern part of the country contain less than 100 ppm of such dissolved solids.

Drinking water standards of the Public Health Service recommend a dissolved solids limit of 500 ppm, but a recent analysis of the United States Municipal Water Supplies showed that:

(1) Water supplies of more than 6,000 communities - their combined population in excess of 40 million - do not meet the recommendations of the Public Health Service in one or more categories.

(2) Some 2,000 communities have water supplies exceeding 1,000 ppm of dissolved solids.

Of the total dissolved solids that may be in the water, the divalent ions cause the most trouble. There are a number of these, but the ones that occur most often in troublesome amounts are:

$$Ca^{++},\ Mg^{++},\ Fe^{++}$$

The divalent ions are called the "hardness ions"; waters containing these ions are known as "hard waters".

Exercise 5

What are some of the difficulties with which you may be acquainted in hard water?

(a)

(b)

(c)

Exercise 6

How could you remove Fe^{++} from water? (Note than Fe^{++} is easily oxidized.)

The removal of Ca^{++} and Mg^{++} is a different matter. The negative ions (anions) with which the hardness ions (cations) are associated are usually:

$$SO_4^{--},\ Cl^-,\ HCO_3^-$$

The calcium and magnesium salts of these anions are all quite soluble. The most insoluble compounds that could be readily and economically formed would be $CaCO_3$, and $MgCO_3$. Both have about the some solubility constant, so let's calculate the solubility of $CaCO_3$ in water:

Exercise 7

What is the K_{sp} expression for the following equation?

$$CaCO_3 \longrightarrow Ca^{++} + CO_3^{=}$$

Exercise 8

If the concentration of Ca^{++} is assumed to be X, what is the concentration of $CO_3^{=}$ in terms of X?

Exercise 9

If the solubility of $CaCO_3 = [Ca^{++}] = [CO_3^{=}]$, what is the solubility of $CaCO_3$, given $K_{sp} = 5 \times 10^{-9}$?

Exercise 10

What is the molecular weight of $CaCO_3$?

Exercise 11

What is the solubility of $CaCO_3$ in grams/liter?

Operating A Water Purification Plant

Background

If a stream, river, lake or pond is the source of the raw water entering a purification plant, all kinds of soluble and suspended solids may be present in the water. For example, the city of Wilmington, Delaware with a population of more than one million people, obtains its raw water from the Brandywine Creek. Hardness is no problem (about 75 ppm) but within the water shed feeding the stream there are eight sewage plants, seven paper mills, one large steel mill, numerous small industries, and thousands of homes that are not connected to a sewer system. Such situations are by no means exceptional; actually, Wilmington may be better situated than many other cities, though less fortunate than some.

What must the chemist do, what chemical and physical processes can he use to convert raw, polluted, turbid water into sparkling clean, bacteria free, good tasting water? In most cases, the chemist needs to know the chlorine demand of the raw water entering the plant. Just what does this mean?

Chlorine Demand

Ammonium compounds and substituted amines are often present in surface waters and these readily react with Cl_2. (If necessary, refer to the mini-course on "The Nitrogen Cycle"). There are many other organic and inorganic contaminants which are oxidized by Cl_2 - for Cl_2 is a powerful oxidizing agent. Such oxidizable pollutants react preferentially with Cl_2, so that no free chlorine is available for killing the bacteria and other micro-organisms in the water to be treated. Therefore, the water chemist must add enough Cl_2 to the raw water to react with the oxidizable substances in the water, plus enough more to kill living organisms. This is expressed as follows:

$$\text{Total } Cl_2 \text{ fed} = Cl_2 \text{ demand} + \text{free } Cl_2$$

The point at which enough chlorine has been added to satisfy the chlorine demand as the break-point.

In the laboratory, the chemist adds a known amount of Cl_2 to a sample of raw water at 20° to 25° C. After waiting for thirty minutes, the unreacted Cl_2 is measured by any of several methods listed in Standard Methods. One of the best and most reliable procedures is amperometric titration. The difference between the amount added and that remaining after thirty minutes is the chlorine demand; this tells the chemist how much Cl_2 to add to the raw water entering the treatment plant.

But there is even more to the story. Many organic compounds are not oxidized by Cl_2, but they are oxidized by $KMnO_4$. As Hugo Victoreen, chief chemist for the Wilmington, Delaware Water Department told me: "if Cl_2 reacts with all the substances from A to M, then $KMnO_4$ reacts with those from K to Z."

The reasons that Cl_2 and $KMnO_4$ are added to water is that they:

(1) Kill micro-organisms (primarily due to the Cl_2).

(2) Promote settling and thus clarification.

(3) Reduce bad tastes and odors.

For one very good reason, $KMnO_4$ is used sparingly - it is expensive. Typically, it may be needed about six months a year when heavy rains or other troublesome conditions burden the raw water with large amounts of pollutants.

Exercise 12

Using the equation:

$$5C_6H_5OH + 28KMnO_4 + 42H_2SO_4 \longrightarrow 30CO_2 + 57H_2O + 14K_2SO_4 + 28MnSO_4$$

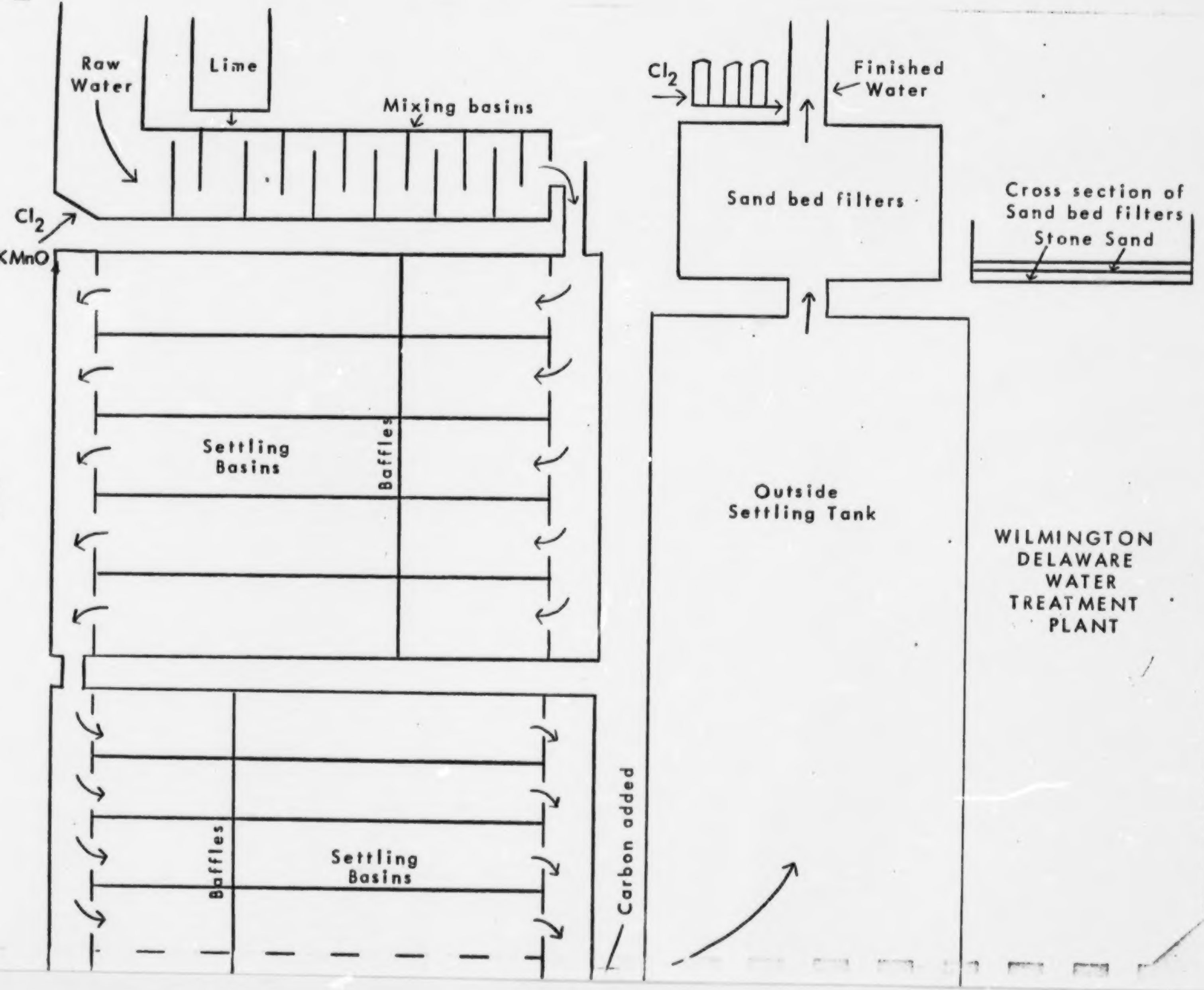
a. If phenol (C_6H_5OH) is found in water at 5ppm, how many pounds of $KMnO_4$ must be added per million gallons of water to remove this compound?

b. At a cost of $3.48 per pound, what would be the cost of $KMnO_4$ for each million gallons?

c. If your monthly bill is $7.00 for 3000 gallons of water, what part of that cost might be due to $KMnO_4$?

OPERATION

So much for the preamble. How does a water purification plant convert raw water into clean, sparkling, bacteria free, good tasting water? The following schematic drawing shows the various operations in the process:


Raw Water
Lime
Mixing basins
Cl_2
KMnO
Settling Basins
Baffles
Settling Basins
Baffles
Carbon added
Cl_2
Finished Water
Sand bed filters
Cross section of Sand bed filters
Stone Sand
Outside Settling Tank
WILMINGTON
DELAWARE
WATER
TREATMENT
PLANT

Step 1 - **Oxidants and alum added**

The oxidants - Cl_2 and $KMnO_4$ - are added to the raw water as it enters the plant. An average dosage might be 3-1/2 ppm of Cl_2 and 1-1/2 ppm of $KMn)_4$, but much more of these may be needed sometimes.

Alum - $Al_2(SO_4)_3$ - is also added immediately to the incoming water. An average figure for this might be 22 ppm, although 45 ppm are sometimes needed.

The above chemicals are mixed thoroughly in the water by passing through baffled mixing basins or by means of mechanical agitators. Both methods are used and both work well.

Step 2 - **$Ca(OH)_2$ added**

The $Ca(OH)_2$ - hydrated lime - is added several minutes after the alum, and it too is thoroughly mixed with the water. An average figure for lime addition is about 9 ppm. Chemically this is added to bring the pH to 7.6, so as to form a precipitate of $Al(OH)_3$ - known as a floc.

Exercise 13

Assuming the water contains $Al_2(SO_4)_3$, what is the balanced equation for the formation of $Al(OH)_3$?

Exercise 14

What is the net ionic reaction for Exercise 12?

Exercise 15

Why should the water be slightly alkaline?

Exercise 16

The retention time of the water in the mixing basin may be an hour or so. Why is this step critical?

Step 3 - **Settling**

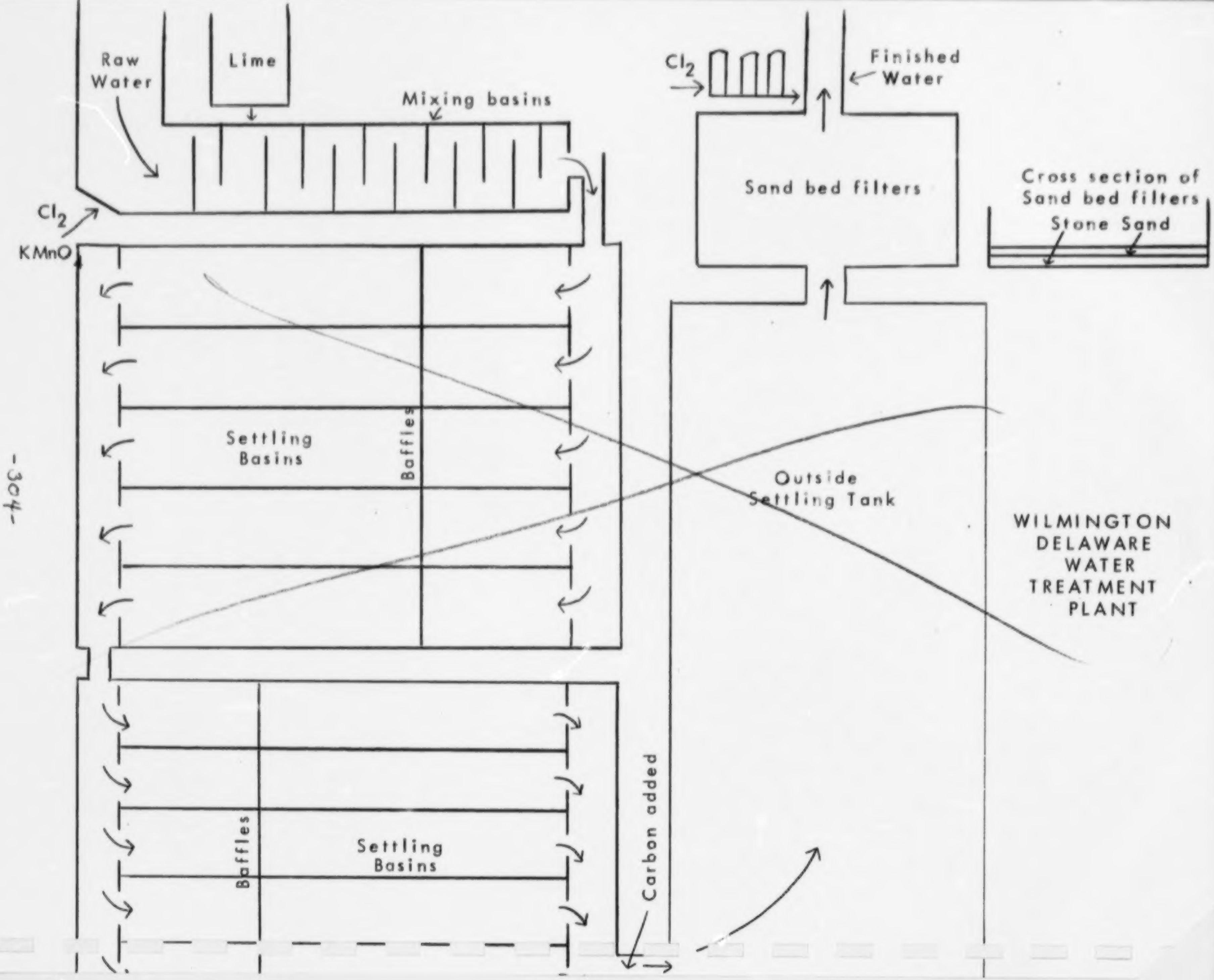
The settling basins are connected in parallel and are fed from a manifold that distributes the water evenly to each basin. The size of the basins must be large enough in relation to the volume of water flowing through them so that gradual settling of the $Al(OH)_3$ flocs occurs. This is why their particle size is so important.

Demonstration 1

A. Make an $Al(OH)_3$ floc in the laboratory and try to filter it. Do this by adding $Al_2(SO_4)_3$ (alum) to water, then add a small quantity of lime $Ca(OH)_2$.

Record the following properties:

1. appearance, including color.


Raw Water
Lime
Mixing basins
Cl_2
$KMnO_4$
Settling Basins
Baffles
Settling Basins
Baffles
Carbon added
Cl_2
Finished Water
Sand bed filters
Cross section of Sand bed filters
Stone Sand
Outside Settling Tank

WILMINGTON
DELAWARE
WATER
TREATMENT
PLANT

2. "feel"

3. does it filter well? Why or why not?

4. does it centrifuge? Why or why not?

B. Repeat the above for a slightly muddy water solution. Record all observations again.

C. Relate this demonstration to a water purification plant.

The flocs of $Al(OH)_3$ are best described as a gelatinous precipitate. They are sticky and they settle slowly, looking something like snowflakes gently falling on a quiet winter evening. And that is precisely why the flocs are effective is clarifying water. As the flocs settle, particles of dirt and solids stick to the gelatinous precipitate and are carried to the bottom of the tank. This downward flow is facilitated by the baffles that extend to about half the depth of the tank and are located neat the entrance end in order to help quiet the flow of water.

A second set of settling tanks provides for more settling of the flocs and thus futher removal of suspended solids.

Exercise 17

In a floc of $Al(OH)_3$, some of the H-atoms can be exchanged for other ions in solution. How can this further aid in purifying water?

Step 4 - Absorption

At this point in the process, activated carbon may be added for the purpose of removing organic contaminants from the water. The carbon used resembles powdered charcoal, it has an extremely high surface area, and it is expensive. Organic compounds tend to be absorbed by the active carbon surfaces and thus removed from the water when the carbon particles are subsequently settled and/or filtered out.

On the average, 3 ppm of activated carbon is effective; because it is expensive, it is only used when necessary.

Step 5 - More settling

The flow sheet shows another very large outside settling tank. If activated carbon is used, most of it settles out in this tank, together with small amounts of other particles that are still in suspension. The more suspended solids that can be removed by settling, the less that need to be removed by filtering.

Step 6 - Filtration

The filters in a water purification plant usually consist of carefully graded gravel or ceramic balls; these are covered with a layer of sand. The sand has an effective grain diameter of about 1/2 millimeter, which means that the spaces between the grains of sand are somewhat smaller. Such a filter is, therefore, incapable of removing very fine particles of solid matter by a simple straining action. The actual mechanism whereby a relatively coarse sand filter can remove very fine solid particles is not yet understood, but it is known that sand filters can only do their work effectively when they are preceded by adequate flocculation and settling.

Periodically, the sand bed filters are back washed to remove the accumulated mud that they collect. This means that the normal downward flow of water is stopped, and a heavy stream of water is introduced at the bottom of the tanks. This is sufficiently turbulent to partially lift the sand and thus free the mud which overflows the top of the tank and thence to the sewer. After a few minutes of back washing, the sand is allowed to settle, and the tank is ready to reuse.

Step 7 - Addition of Cl_2 and F^-; corrosin control

The above steps produce water that is sparkling clear, bacteriologically safe, and tastes good. To insure that is remains so by the time it reaches the ultimate user, many water plants add Cl_2 to the finished water so that is contains about 1 ppm of free Cl_2.

Some localities require that sodium silico fluoride be added in the amount of 1 ppm of F^-.

The amounts of chemicals used throughout the above various steps are adjusted so that the finished water has a pH = 7.6. Such slight alkalinity is very effective in reducing the corrosive action of the water on metals.

Exercise 18

Explain the following and suggest corrective procedures:

a. Slow water flow through filter bed

b. The finished water, upon standing, has a corrosive effect on metal containers.

c. Bacterial count still high.

d. Solid particles are found in the drinking water.

Purifying Water By Reverse Osmosis

Both anions and cations can be removed from water by a process known as reverse osmosis.

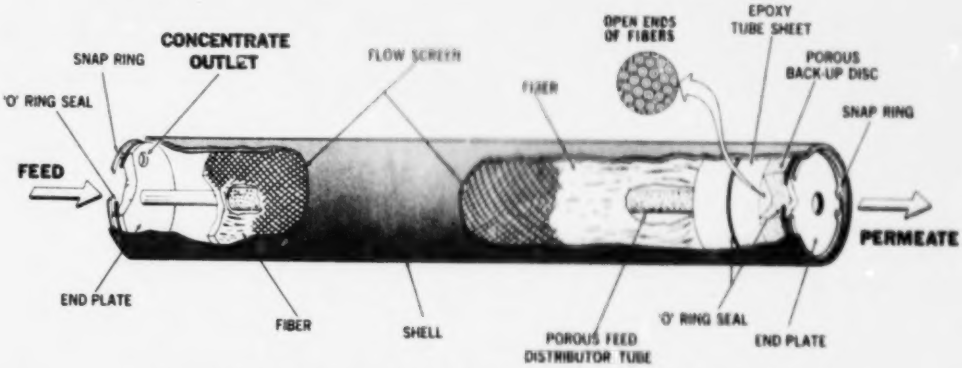
Osmosis is a natural process whereby small molecules pass through the pores of a semipermeable membrane that, at the same time, block the passage of larger molecules. This is what happens in our digestive system. The food we eat is broken down by enzymes until the fragments are small enough to pass through the walls of the small intestine. The blood picks of these nutrients and carries them throughout the body.

The driving force that naturally pushes the small molecules through the pores of the semipermeable membrane is known as osmotic pressure; the flow of the solute particles is from a dilute into a more concentrated solution, thereby diluting the latter until eventually the solutions are of equal concentration on both sides of the membrane.

Reverse osmosis is the opposite of the natural process. That is, instead of water flowing into a more concentrated solution, purified water is driven out of a solution containing dissolved substances. Relatively high pressures of 400 to 800 pounds per square inch (psi) are needed to do this.

Reverse osmosis is a new water treatment process of great potential importance in reducing the salinity of brackish water supplies. Increased population in areas that lack sufficient good water - Florida, for example - is forcing the utilization of previously unusable supplies by new technology.

Commercially, the application of reverse osmosis for purifying water is becoming a flourishing business; to date, the DuPont Company is a leader in the field. They have developed hollow fibers made of an aromatic polyamide that are thinner than a human hair. A pressure vessel containing these fibers is called a permeator; this is shown in the following sketch:


CONCENTRATE OUTLET
SNAP RING
'O' RING SEAL
FEED
FLOW SCREEN
OPEN ENDS OF FIBERS
EPOXY TUBE SHEET
POROUS BACK-UP DISC
FIBER
SNAP RING
PERMEATE
END PLATE
FIBER
SHELL
POROUS FEED DISTRIBUTOR TUBE
'O' RING SEAL
END PLATE

CUT AWAY DRAWING OF PERMASEP® PERMEATOR

To prevent clogging the spaces between the fibers, raw water is pretreated as follows:

(a) It is filtered to remove suspended solids that might cause trouble.

(b) H_2SO_4 is added until the pH = 5.5. This converts bicarbonates to CO_2, thus avaoiding the possibility of precipitating $CaCO_3$; in addition, Fe^{++} is kept in solution.

The pretreated water is pumped into the pressure vessel and flows around the outside of the hollow fibers. The fibers are looped at one end and open at the other. The open ends are encased in a plastic seal which separates the feed water from the good water. So it is that, by reverse osmosis, dissolved solids are removed brom the water. Said somewhat differently, high pressure pushes water molecules through the pores of enormous numbers of tiny hollow filaments, pores so small that the solute ions and molecules (dissolved solids) are unable to squeeze through.

After passing through the permeator, the purified water is aerated to remove CO_2, the pH adjusted to 7.5, and Cl_2 added. Overall, 90% of the dissolved salts are removed from the raw water. The following table shows how effective the procedure has proven to be in a municipally owned plant in Greefield, Iowa:

	Pretreated feed	Actual product
Calcium	150	1.4
Magnesium	45	0.4
Sodium	474	38
Potassium	24	1.8
Bicarbonate	81	65
Sulphate	1,125	17.5
Chloride	335	17.2
Fluoride	1	0.2
Nitrate	0.9	0.06
Silica	7	0.05
Iron	2.2	0.05
Manganese	0.02	0.02
Phosphate	16.2	0.18
Conductance	3,000	220
pH	5.7	7.5
Hardness	560	5.0
TDS	2,250	142

Greefield, Iowa is a small community of 2,200 people, so the above plant is designed to produce 150,000 gal./day. The plant superintendent states, "Everyone in Greefield is pleased with the high quality of water available at all times regardless of rainfall. The reverse osmosis system has given product water in greater quantity, better quality, and at lower cost than estimated or guaranteed. There is no doubt, therefore, that this plant can demineralize brackish water economically and reliably. No community needs to accept water that does not meet USPHS water quality recommendations."

A reverse osmosis plant has been authorized for installation at Venice, Florida. Its capacity will be 1,000,000 gals./day. So it is that advanced technology meets the needs of an expanding society. Treating water by reverse osmosis costs 65¢ per 1,000 gals., which is greater than for water that needs no treatment and is merely pumped from an underground well; but the price is quite acceptable for something as essential as good, clean, drinking water.

Exercise 19

Reverse osmosis is a technique that has been known for some time but not used commercially until recently. Why?

Ion Exchange

Many homes in rural areas have driven or dug wells which supply water that is excessively hard. About the only practical way an individual home owner can remove hardness ions from water is by the use of an ion exchanger. This is a relatively inexpensive installation that utilizes a natural mineral called Zeolite. There are now many synthetic ion exchange resins on the market that perhaps perform better than Zeolite, but this is the material that was used first and thus is better known.

Zeolite looks like a coarse green sand, but actually it is a porous crystalline mineral that has a very large surface area. Chemically, it is sodium aluminum silicate - $NaAlSiO_4^-$ - and the sodium is present in the crystal as loosely bound Na^+ sodium ions.

Exercise 20

If we consider sodium Zeolite as Na^+Z^-, write the equations for the reaction of:

(a) Ca^{++} with Na^+Z^-

(b) Mg^{++} with Na^+Z^-

(c) Fe^{++} with Na^+Z^-

When water containing hardness ions is passed through a bed of Zeolite, the Na^+ are replaced by Ca^{++}, Mg^{++}, and Fe^{++} and thus removed from the water. This means that the water now contains Na^+ instead of the hardness ions, but let's see what happens. Hardness equivalent to 2,000 ppm is considered excessive.

Exercise 21

2,000 ppm equals how many % ?

This amount of Na^+ in water is hardly noticeable and certainly not objectionable.

Exercise 22

Would you expect an ion exchanger to remove anions from the water?

Exercise 23

How would you regenerate the sodium Zeolite ion exchanger?

Exercise 24

What is the balanced equation for the regeneration of sodium Zeolite? (Na^+Z^-)

The accompanying sketch shows a cut-away flow diagram of a typical ion exchanger. The steps taken during a complete cycle are as follows, such an installation can be operated manually or automaticallly by a timer.

(a) Service flow

Valves 1 and 2 open; all other valves closed. The length of satisfactory service depends upon the volume of water used and the quality of the water treated.

(b) Back wash

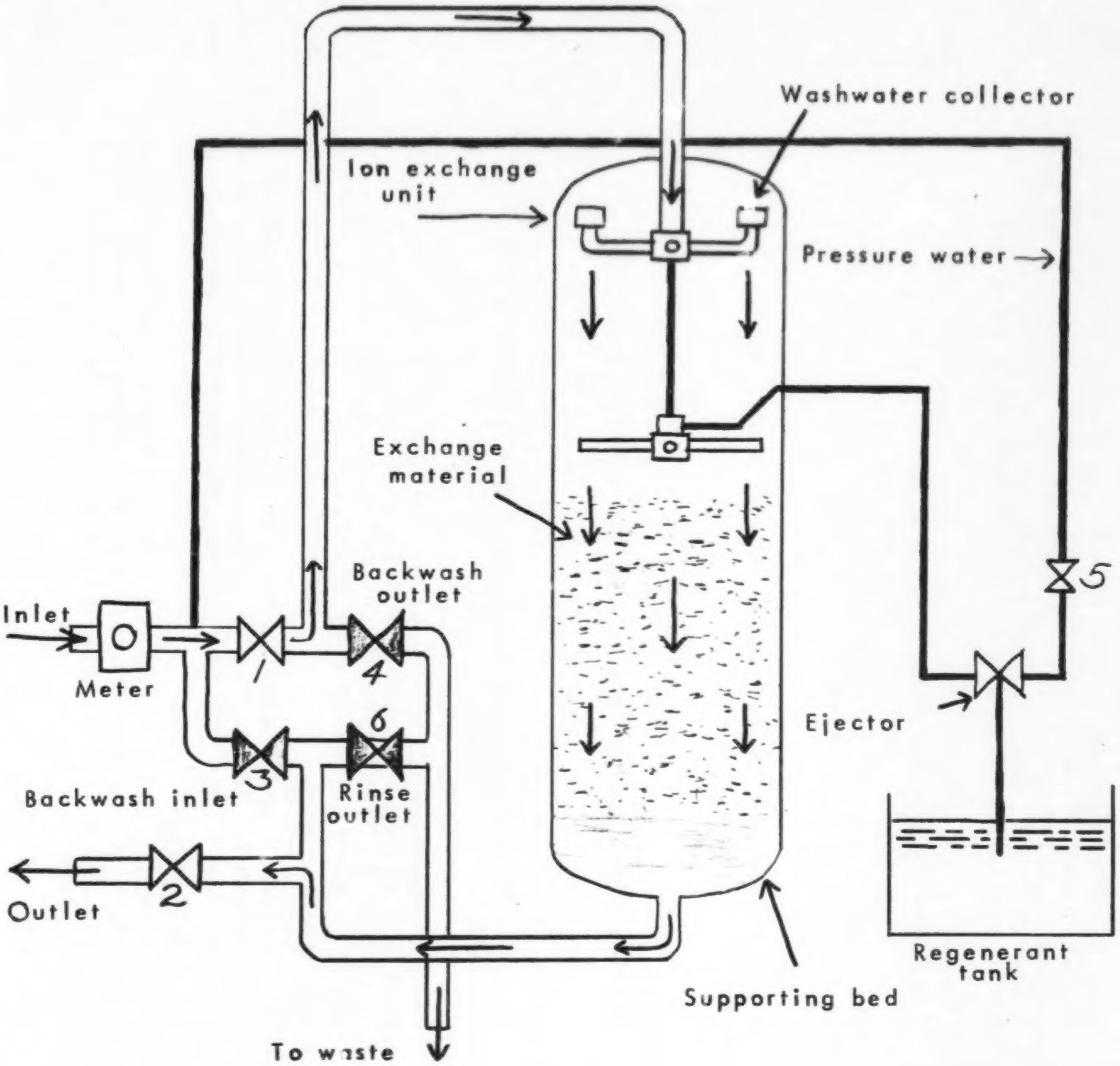
Valves 3 and 4 open; all others closed. This operation takes but a few minutes; the flow of water should be carefully regulated so as to prevent carry-over of the Zeolite.

(c) Regeneration

Valves 5 and 6 open; all others closed. The vendor of the ion exchanger will advise regarding this step.

(d) Rinse

Valves 1 and 6 open; all others closed. The purpose of this is to remove the excess saltfrom the Zeolite bed; a little experience will soon indicate how long to do this.


Washwater collector
Ion exchange unit
Pressure water
Exchange material
Backwash outlet
Inlet
Meter
1
4
6
3
5
2
Ejector
Backwash inlet
Rinse outlet
Outlet
Regenerant tank
Supporting bed
To waste

TYPICAL ION EXCHANGER showing service flow with valve nest regeneration - backwashing, injecting, chernicals, rinsing

Exercise 25

Sodium Zeolite is $NaAlSiO_4$. 100 pounds of this material is placed in a water line. If water containing 200 ppm Ca^{++} is run through the exchanger at a rate of 1000 ml/min., how many gallons of water could be "deionized" before regeneration is needed?

Exercise 26

How many pounds of NaCl would be needed to completely regenerate the "used up" sodium Zeolite tank?

Demonstration 2

On the demonstration bench is a small ion-exchanger resin and equipment to measure conductivity. Take 50 ml samples of tap water, distilled water, and lake or stream water. Measure the conductivity of each, then pass through the ion-exchanger. Remeasure the conductivity. Explain your results.

ANSWERS

A. Pretest

1. See pages 298.

2. a. Excessive use for irrigation has left some rivers (the Colorado) too salty for use.

   b. Municipal and commercial wastes have polluted great rivers and lakes to the point of rendering them virtually useless. (Lake Erie).

   c. Underground reservoirs of water are being depleted.

3. See page 300.

4. Fe^{+2}, Mg^{+2}, and Cu^{+2} are most common, other +2 ions may also contribute.

5. $Ca^{++}\ CO_3^{=} = 5 \times 10^{-9} = X^2$

$$x = 7 \times 10^{-5} \text{ mole/1 of } Ca^{++} = M$$

$$ppm = 7 \times 10^{-5} \text{ mole/1} \times 100 \text{ S/mole} \times \frac{1 \text{ ppm}}{1 \times 10^{-3} \text{ g/1}} = 7 \text{ ppm}$$

6. Several ways possible with ion exchange being best and easiest.

7. Ca^{++} would cause precipitation of soaps and be a nuisance, but causes no health problems.

8. See page 302.

9. See pages 304 and 305.

10. a. $Fe^{+2} + 2Na^{+}Z^{-} \longrightarrow Fe^{+2}Z^{-2} + 2Na^{+}$

    b. $2000 \text{ lbs. } Na^{+}Z^{-} \times \frac{2 \text{ lb } Na^{+}}{100 \text{ lb } Na^{+}Z^{-}} \times \frac{56 \text{ lb } Fe^{+2}}{2(23) \text{ lb } Na^{+}} =$

    $40 \text{ lb } Fe^{+2}$ removed.

    c. $40 \text{ lb Fe} \times \frac{454 \text{ g}}{1 \text{ lb}} \times \frac{\ell}{50 \times 10^{-3} \text{ g}} = 3.6 \times 10^{5}$ liters.

B. Study Guide

Exercise 1

(a) Much of the United States is desert devoid of any appreciable amount of rainfall. Large areas of the Mid-West are marginal for farming because of inadequate rainfall. These were the regions that caused the dust storms during the drought of the 1930's.

(b) Mountainous areas are extremely valuable for many reasons. Their forests provide lumber, their rugged terrain is beautiful and the sites of many of the nation's most beautiful park lands. Their lakes and reservoirs collect, store and act as distribution centers for much of the nation's water supply - both for underground and surface rivers.

(c) In seeking the sea, water from mountain lakes and reservoirs often flows underground. These sometimes break the surfaces as springs, or can be tapped by drilling wells. Deep underwell pools are not infrequent, and these act as excellent source of good drinking water for those places fortunate enough to find them.

Exercise 2

(a) Pumping water "as is" involves little chemistry other than constant vigilance to make sure that it is not contaminated.

(b) The transportation of water through huge aqueducts to distant points and then distributing it to millions of customers is no small engineering feat.

Exercise 3

Riding water of mud, silt, organic debris - and the many organisms associated therewith - is the task of a water treatment plant. It must remove the suspended solids that the streams or river pick up or has dumped into it.

Exercise 4

The amount and content of such burdens changes from day to day as a result of heavy rains and subtly with the change of seasons due to leachings from forests and farms. Then there is the accidental spillage that may cause serious health or taste problems. To remove such contaminants is perhaps the greatest challenge facing the water chemist; the pat rules of the text book are often inadequate in such cases, but require the skill, experience, and ingenuity of a really competent chemist.

Exercise 5

Hard waters form a ring in the bath tub, prevent foams from forming in the kitchen sink, cause iron stains, have an unpleasant taste, and deposit scale in the furnace and water pipes. In other words, hard water is a nuisance.

Exercise 6

Removing dissolved iron from the water is relatively easy since Fe^{++} is readily oxidized to Fe^{+++}, which then hydrolyzes to form insoluble $Fe(OH)_3$ - iron rust. This is subsequently removed by settling and/or filtration.

Exercise 7

$$K_{sp} = [Ca^{++}][CO_3^{=}]$$

Exercise 8

Since $[Ca^{++}] = X$, then $[CO_3^{=}] = [Ca^{++}] = X$

Exercise 9

$$K_{sp} = 5 \times 10^{-9} = [Ca^{++}][CO_3^{=}] = [X][X] = X^2$$

$$X^2 = 5 \times 10^{-9} \text{ or } 50 \times 10^{-10}$$

$$X = \sqrt{50 \times 10{-}10}$$

$$X = 7 \times 10^{-5} \frac{\text{moles}}{\text{liter}}$$

Exercise 10

$$\begin{array}{llll} CaCO_3 = & 1\ Ca & 40 = & 40 \\ & 1\ C & 12 = & 12 \\ & 3\ O & 16 = & \underline{48} \\ & & & 100\ \text{g/mole} \end{array}$$

Exercise 11

$$\frac{7 \times 10^{-5} \text{ moles}}{\text{liter}} \times \frac{100 \text{ g}}{1 \text{ moles}} = 7 \times 10^{-5} \text{ g/liter}$$

Exercise 12

a. $10 \text{ gallons} \times \frac{8.3 \text{ lb } H_2O}{1 \text{ gal}} \times \frac{1 \text{ lb } C_6H_5OH}{10^6 \text{ lb } H_2O} \times \frac{28(158) \text{ lb } KMnO_4}{5(94) \text{ lb } C_6H_5OH}$

$= 78$ lb $KMnO_4$ per million gallons.

b. $\text{cost} = 78 \text{ lb } KMnO_4 \times \frac{\$3.48}{\text{lb } KMnO_4} = \$271.00.$

c. $\text{cost per 3000 gal} = \frac{\$271}{\text{million}} \times .003 \text{ million gal} = \$0.81$

$\% = \frac{.81}{7.00} \times 100 = 12\%$

Exercise 13

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2\ Al(OH)_3 + 3\ CaSO_4$$

Exercise 14

$$Al^{+++} + 3\ OH^- \longrightarrow Al(OH)_3 \downarrow$$

Exercise 15

To insure complete precipitation.

Exercise 16

The retention time of the water in the mixing basin may be an hour or so. This step is critical since the amount and severity of agitation determines the size of the $Al(OH)_3$ flocs, which is so essential to the effectiveness of the next step.

Exercise 17

The $Al(OH)_3$ can act somewhat like an ion-exchange resin, removing other cations as it settles from the water.

Exercise 18

(a) Blocked filter bed - back flush it.

(b) pH too low - adjust it to pH 7.6.

(c) Add Cl_2.

(d) $Al(OH)_3$ floc not working - add more $Ca(OH)_2$, adjust pH - increase retention time in settling basin.

Exercise 19

The cost has been prohibitive. With increased demands for water and increased costs for cleaning water by traditional means, the cost of reverse osmosis is now more competitive.

Exercise 20

(a) $Ca^{++} + 2\ Na^+Z^- \longrightarrow CaZ_2 + 2\ Na^+$

(b) $Mg^{++} + 2\ Na^+Z^- \longrightarrow MgZ_2 + 2\ Mg^{++}$

(c) $Fe^{++} + 2\ Na^+Z^- \longrightarrow FeZ_2 + 2\ Na^+$

Exercise 21

$2{,}000\ ppm = 2{,}000 \times 10^{-6} = 2 \times 10^{-3} = 0.002 = 0.2\%$.

Exercise 22

An anion exchange resin will remove anions from water. Sodium Zeolite will not remove anions such as Cl^-, $SO_4^=$, and HCO_3^-. These ions remain in solution and cause no major problems.

Exercise 23

After a certain volume of water has passed through the ion exchanger, all the Na^+ of the Zeolite will be replaced by the hardness ions; in addition, the sand-like bed tends to filter out suspended solids. When this happens, the unit is back washed to remove the solid particles and loosen the bed of Zeolite. Then a concentrated solution of NaCl is passed through the Zeolite; this high concentration of salt displaces the hard ions and restores the Na^+ to their original sites. The excess NaCl solution is rinsed away with fresh water; the Na^+ on the Zeolite are so tightly held that they are not disturbed. The back wash and rinse waters are led to a drain. Thus, the unit is rejuvenated and made ready for another cycle.

Exercise 24

$MgZ_2 + 2\ NaCl \longrightarrow 2\ NaZ + MgCl_2$

or $MZ_2 + 2\ NaCl \longrightarrow 2\ NaZ + MCl_2$

Exercise 25

Mol. wt. of $NaAlSiO_4 = 142$

$\frac{23}{142} = 16.2\%$ Na

Exercise 25 (con.)

$100\text{ lbs.} \times .162 = 16.2\text{ lbs. of } Na^+ \text{ in Zeolite.}$

$16.2 \times \frac{40}{23} = 28.2\text{ lbs. of } Ca^{++}$, equivalent to 16.2 lb. Na^+

$1/2 \times 28.2 = 14.1\text{ lbs. of } Ca^{++}$ available for absorption, based on ion equivalents.

$14.1 \times 454 = 6{,}400\text{ g. of } Ca^{++}$

$200\text{ ppm} = 200 \times 10^{-6} = .2 \times 10^{-3} = .2\text{g/l}$

$\frac{6{,}400\text{g}}{0.2\text{g/l}} = 32{,}000\text{ l.}$

$\frac{32{,}000\text{ liter}}{3.785\text{ gal./liter}} = 8{,}500\text{ gal.}$

Exercise 26

$16.2\text{ lbs. } Na^+ \times \frac{58.5}{23.0} = 41.3\text{ lb. of NaCl}$, theoretically needed for regeneration.

Actually, almost twice as much NaCl must be used since the interstices of the granular Zeolite holds a quantity of the salt brine that is later rinsed away.

WASTE WATER TREATMENT

SUMMARY

There is little new so far as sewage treatment is concerned. A well designed and operated waste water treatment plant depends upon Nature to do the job on a large scale that the out-house did - and does - down on the farm.

There are three levels of sewage treatment: a) primary, b) secondary, and c) tertiary. More and more communities are going as far as secondary treatment; few are yet using the third step because of increased expense.

The operations of a sewage plant are aimed at removing settleable solids from the raw waste water, and reducing the B.O.D. to as low a level as possible. More and more the E.P.A. is demanding that the effluent water from a sewage plant be treated with sufficient Cl_2 to kill fecal coli.

PREREQUISITES

Before beginning this mini-course, you should be able to:

1. When given suitable data, calculate the B.O.D. and C.O.D. of a water sample in ppm.

2. State from memory that 1 gallon of water weighs 8.35 lbs., and use this value to calculate the total weight of water in a given volume.

3. Use percentage to calculate parts when given a total quantity of a sample.

ACKNOWLEDGMENT

Mr. Thomas Rooney, Sanitary Engineer for the City of Wilmington, Department of Public Works, was extremely helpful and thorough in going over the operations and details concerning the Wilmington, Delaware waste water treatment plant. His cooperation and unselfish contribution of time and knowledge is greatly appreciated.

Mr. Henry H. Gunther, Kent County Sanitary Engineer was equally competant and gracious in explaining the operations of his new plant in Kent County, Delaware.

Dr. Donald Wilkinson, associate professor of chemistry at Delaware State College, recommended and inserted the exercises in this mini-course.

OBJECTIVES

After completion of this mini-course, you should be able to:

1. Define: primary treatment
   secondary treatment
   tertiary treatment

2. Describe the technique for each of the following and the effects expected upon water quality for each.
   (These descriptions should include
   the equipment used, the difference
   between small and high volume

treatment plants, and a statement of the expected improvement in B.O.D., C.O.D., and suspended solids for each stem.)

I. Primary treatment
  a. screening
  b. grit removal
  c. primary clarification

II. Secondary treatment
  a. aeration
  b. final settling basins
  c. chlorination
  d. thickening
  e. digesting
  f. polishing ponds

III. Tertiary treatment

WASTE WATER TREATMENT

There is little new under the sun as far as sewage treatment is concerned. Our forefathers - and most people of today - just poured their domestic wastes into a nearby ditch or a hole dug in the ground. Nature did the rest. Actually, it was a satisfactory way of handling domestic wastes for the land was vast and the people few. Where these conditions still exist, the old fashioned out-house may still serve as a place of comfort and retreat. Even so, not many of us would relish the idea of returning to this aspect of the good ole days.

Not many of us appreciate what happens to our waste when we take a shower, flush a toilet, use a disposal, or wash our clothes and dishes. We take this essential service for granted and perhaps we should. More and more, of late, the problems of water and air pollution, and solid waste disposal have been frontpage news items, because the handling of wastes - domestic and industrial - are serious and costly matters that concern our health and our pocketbooks.

This mini-course is devoted to the handling of waste-water. With few exceptions, a well designed and operated sewage treatment plant depends upon Nature to do most of the job on a large scale that the out-house did - and does - down on the farm.

Waste-water from homes, small and large buildings, small and large industries, is collected by a maze of sewer pipes that grow ever bigger as they approach and eventually pour their accumulated burden into the sewage treatment plant. Some of these plants are old, some new, and most are undergoing modernization and expansion. But in all cases, one of two basic processes is used - and will be described - depending upon the volume of waste-water that must be handled. Obviously, too, there is no sharp line of demarcation between what is a large and a small volume of water.

Since Wilmington, Delaware is home grounds for the author, its sewage treatment plant will be described as typical of those handling large amounts of combined domestic and industrial sewage. Actually, plants serving larger cities would probably use the same equipment, only more of it in proportion to their needs. The Wilmington plant is also typical in that it is an old plant that has recently completed one major expansion and remodeling, with additional improvements authorized and underway to meet the stricter E.P.A. standards.

Large Volume Sewage Treatment Plant

As waste-water is collected over a large area, it goes through pumping stations which force the water to its destination. Usually, there are coarse screens with 3" openings ahead of the pumps to remove large objects such as rags, sticks, leather, etc.

There are three levels - or stages - of waste-water treatment, but only the first two are presently used to any extent;

(1) Primary, (2) Secondary, (3) Tertiary.

The primary stage removes solids.

Exercise 1

How, do you believe, the primary stage removes solids?

Exercise 2

If a plant only has a primary stage, what would happen to the water?

Exercise 3

After removing studge, water should go to a secondary stage. What do you believe would be the purpose of this stage?

Exercise 4

Obviously, the tertiary stage is a finishing stage. What do you believe would be the purpose of this stage?

Now let's examine each of the above in more detail.

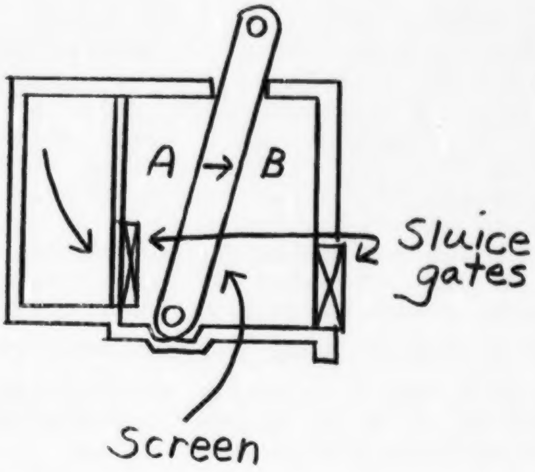
PRIMARY TREATMENT

The raw sewage (50% domestic and 50% industrial) entering a typical treatment plant might average 400ppm of biodegradable and suspended solids. It can be assumed that 1/2 of this is B.O.D. and the other 1/2 is inert. Thus there would be:

	Biodegradable and suspended solids	
	B.O.D.	Suspended solids
Raw sewage	200ppm	200ppm

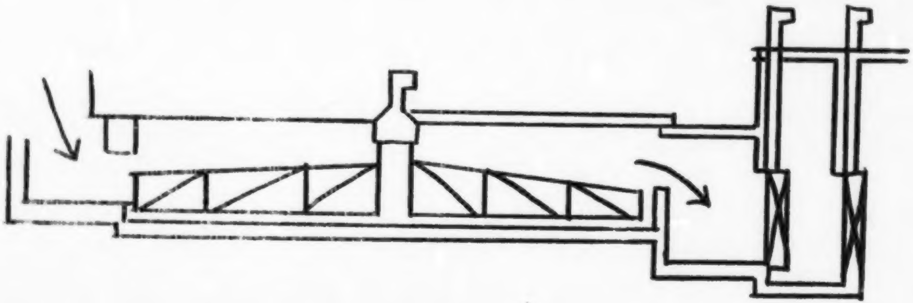
Screening

Rags, leather, plastics, sticks and stones that passed through the screens at the pumping stations are removed by finer screens as the sewage enters the plant. In going from A to B, an inclined moving screen with 3/4" openings removes large objects and dumps them into a waiting truck.



Grit removal

The water then enters the top of a tank such as:



The gravel and coarse sand settle to the bottom of the tank where they are removed by rakes which sweep the solids to an exit in the side of the tank. These solids plus those removed by the screens are hauled to a land-fill. These amount to about 5% of the B.O.D and 10% of the non-biodegradable suspended solids contained in the raw sewage:

	Biodegradable and suspended solids	
	B.O.D.	Suspended solids
Raw sewage	200ppm	200ppm
After screening and grit removal	190	180

Finding suitable dumping sites sometimes poses a problem.

Exercise 5

Since the initial screening removes only 5% of the B.O.D. and 10% of suspended solids would it not seem logical to eliminate this step?

Primary clarification

The overflow from the grit removal tank is then piped under and up through the center of a very large tank where it is discharged at the top and center of the tank. A typical clarification tank is 160' in diameter, 11.5' deep and holds two million gallons of water. The retention time is about two hours, so that the flow from the center to the overflow weirs at the perimeter allows much of the suspended solids to settle to the bottom of the tank. As the following sketch shows, the bottom slopes toward the center so that the settled solids are swept by slowly revolving rakes to and through an underflow opening.

The water overflowing the effluent weirs is relatively clear.

Three such tanks as shown on the next page can handle ninety million gallons of water a day. Greater volumes of water can be treated by installing more such tanks.

Primary clarification removes about 25% of the B.O.D. and at ninety million gallons per day this amounts to:

$$90\times10^{6}\ \text{gal.} \times 8.35\ \text{lbs./gal.} = 750\times10^{6}\ \text{lbs.}$$

$$200\times10^{-6} \times 750\times10^{6} = 150{,}000\ \text{lbs./day of B.O.D.}$$

Since the overflow of the clarifiers is relatively clear water, this means that the 112,500 lbs. of remaining B.O.D. is present mostly as dissolved substances and colloidal solids.

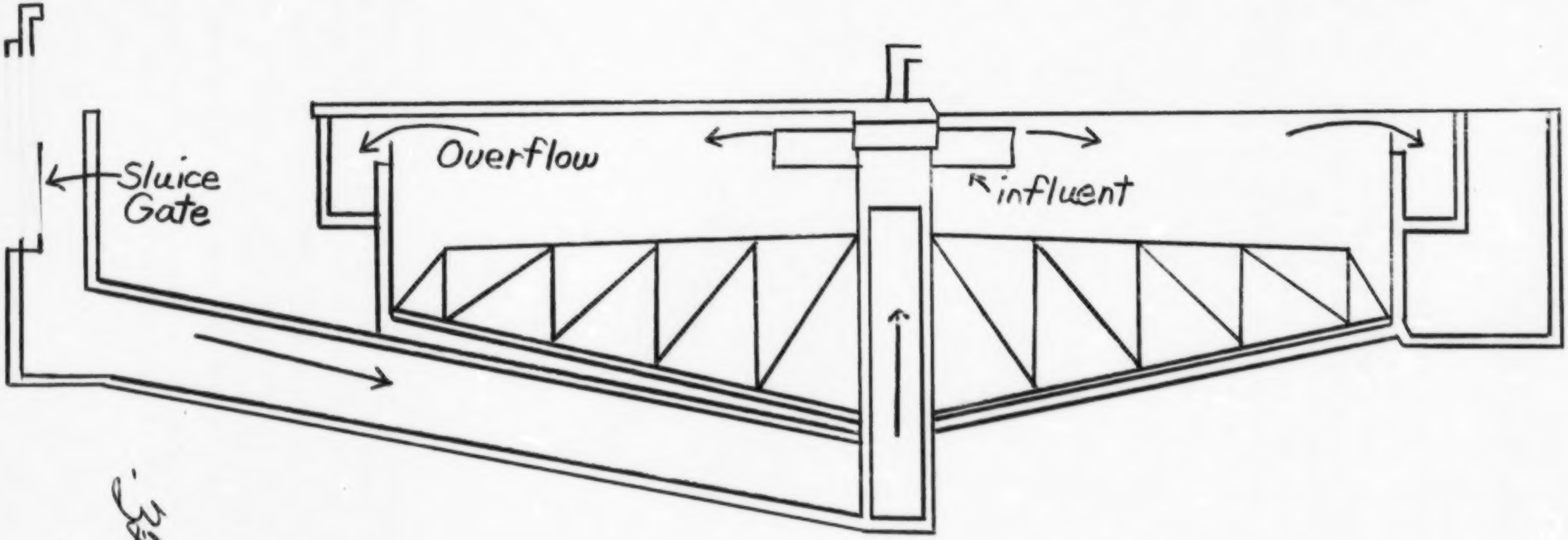
Primary clarification also removes about 100ppm of biologically inert solids, so at this point there is:

	Biodegradable and suspended solids	
	B.O.D.	Suspended solids
Raw sewage	200ppm	200ppm
After screening and grit removal	190	180
After primary clarification	140	80

Exercise 6

Suggest some problems that might have arisen if one did not include the initial screening?

Reproduced from best available copy.

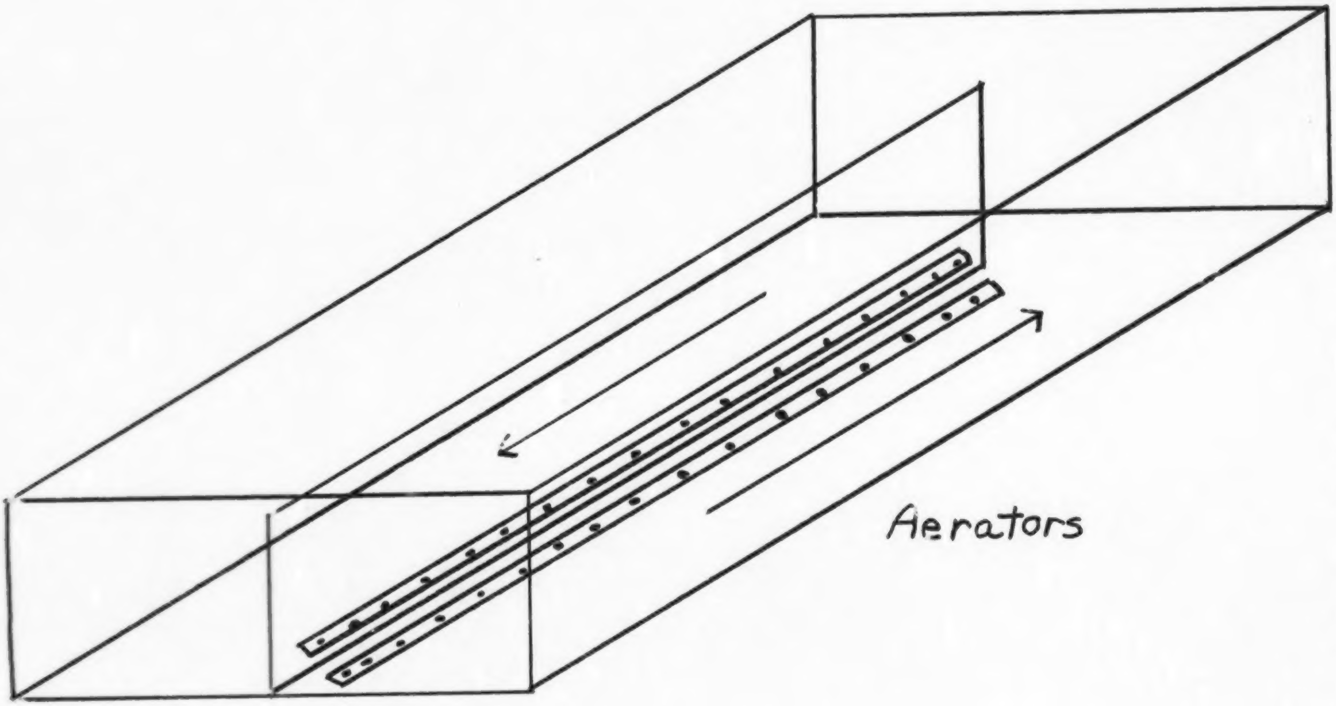

Sluice Gate
Overflow
influent

Primary clarifier

SECONDARY TREATMENT

Aeration

The overflow from the primary clarifiers is then distributed to six aeration basins. These are large rectangular tanks, and each might be 260' long, 60' wide, and 15' deep; have a capacity of 1,610,000 gallons; have a retention time of about two hours. Each basin is divided into two sections so that the water passes the length of the tank twice before being discharged. These six basins can handle ninety million gallons a day. Additional tanks would be needed to treat larger amounts of water.



Perforated pipes along the sides and bottom of the tank add high pressure air from seven 250 H.P. blowers. The resulting turbulance borders on the spectacular, so that pipes along the top of the basins spray water to inhibit excessive forming.

Two objectives are accomplished by this operation:

(a) the extreme turbulance results in the growth of particle size so that some of the colloidal matter coalesces and thus subsequently settles out;

(b) the aeration promotes the reduction of B.O.D. due to the action of aerobic bacteria.

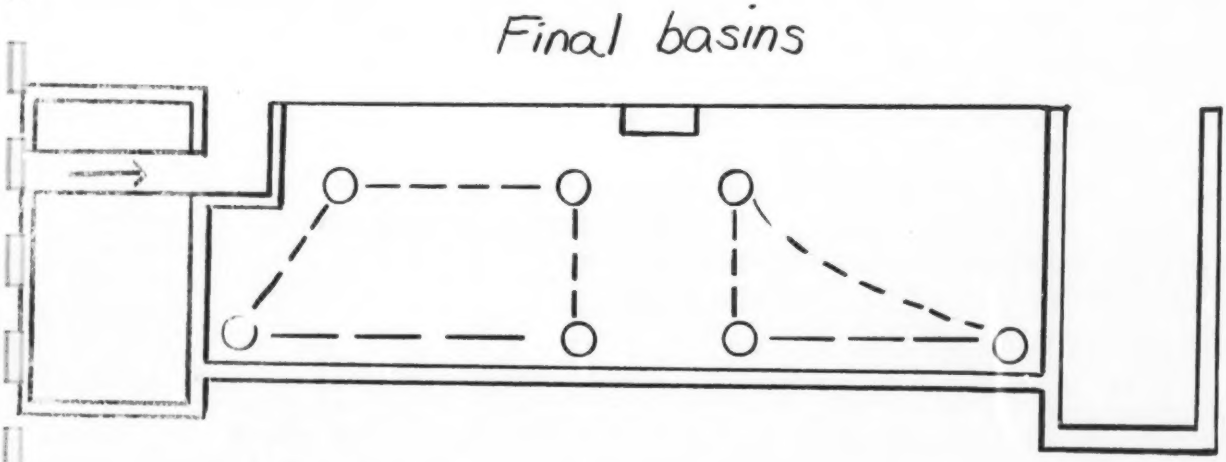
Exercise 7

Chemically speaking, what is the purpose of the aeration procedure?

Final Settling Basins

After aeration, the water enters six large rectangular tanks and each: is 340' long, 61.5' wide and 12' deep, holds 1,880,000 gallons; has a retention time of 3'1/2 hours.

As a result of the previous vigorous aeration, some of the fine particles coalesce so that solids settle out as the water slowly traverses these final settling basins. Traveling baffles attached to a conveyor slowly move along the surface of the water thereby pushing surface scum to an overflow weir at one end of the tank. As shown in the sketch, the baffles return to the discharge end by scraping along the bottom of the tank, where the settled solids are discharged and returned to the aeration basins.



FINAL BASINS

As a result of aeration and traversing the final settling basins, the B.O.D. is reduced by an additional 45% as based on the influent raw sewage. That is, overall, 75% of the initial B.O.D. is removed by the primary and secondary treatment steps, so, 0.25x200 = 50ppm of the B.O.D. remains. About 15% of the biologically inert solids are also removed during secondary treatment so that:

	Biodegradable and suspended solids	
	B.O.D.	Suspended solids
Raw sewage	200ppm	200ppm
After screening and grit removal	190	180
After primary clarification	140	80
After secondary treatment	50	50

Chlorination

As a final step before discharged into a river, stream or lake, Cl_2 is added to the above effluent water.

Exercise 8

What controls the amount of chlorine that is added to the water?

Thickening

The sludge going to the digestors consists of the:

(a) 150ppm of suspended solids removed during primary and secondary treatment:

$$200 - 50 = 150\text{ppm}$$

(b) B.O.D. solids.

This requires a bit of explanation. During aeration, the bacteria grow on the organic matter, partially converting it to CO_2 In so doing they grow and multiply in number and their bodies add to the solids that are removed in the final settling basins. The net result is about 50% reduction in settleable solids As noted above, secondary treatment removed:

$$140 - 50 = 90\text{ppm of B.O.D.}$$

Thus the total is:

$150 + 45 = 195$ppm of settleable solids entering the digestors.

On the basis of ninety million gallons of raw sewage, this amounts to.

$$190\text{x}10^6 \text{ gal. x } 8.35 \text{ lbs./gal.} = 750\text{x}10^6 \text{ lbs.}$$

$750\text{x}10^6 \text{ x } 195\text{x}10^{-6} = 145{,}000$ lbs./day of settleable solids going to the digestors.

Digestors are large totally enclosed tanks, 90' in diameter and 30' deep. Each has a capacity of 1,365,000 gallons; four such tanks handle the above sludge.

As the sketch on the next page shows, the sludge is circulated and heated to maintain a temperature of about 95° F. which is optimum for the growth of anerobic bacteria. The sludge is continuously fed to and removed from the digestors, the average retention time being about 25 days. Since the system operates under anerobic conditions, the by-product of the bacterial action is CH_4.

This combustible gas provides the heat for maintaining the temperature in the tank.

At 145,000 lbs./day and a retention time of 25 days, this amounts to about:

145,000 x 25 = 3,625,000 lbs. of solids (dry basins)

The digestive process reduces the above amount to about 2,000,000 lbs. which contains about 14% solids, so that 14,000,000 lbs = 7,000 tons of stabilized material is disposed of in a landfill.

The main purpose of the digestors is to stabilize the solids which, in lay language, means to minimize objectionable odors.

Polishing Ponds

The construction of large acreage "polishing ponds" has been authorized; they are scheduled for completion by mid 1976. These ponds provide for the prolonged aeration of the overflow from the final settling basins. To do this, the ponds will be equipped with floating mechanical aerators that will provide the O_2 for additional aerobic activity. Thus the total reduction in B.O D. for the entire plant is designed to be in excess of 90%.

The effluent from the polishing ponds will be treated with Cl_2.

Small Volume Sewage Treatment Plant

The recently built waste-water facility of Kent County, Delaware treats five million gallons of sewage a day so it is considered a relatively small plant; actually, it is designed to handle twice this amount. The extra capacity is provided since, at present, only five communities with a total population of 55,000 people are being served. Experience shows that, once such facilities are available, other areas are encouraged to use them

The processes used by this plant differ significantly from those of the Wilmington plant so this is one reason for using it as an example. However, the two plants have one all important common denominator: they both depend upon Nature to do most of the job. They differ primarily in that the large plant must find ways of somehow coping with large volumes of liquids. As noted above, this is done by settling out the suspended solids so that the water can be cleansed as quickly as possible, chlorinated and discharged. The small plant that will now be described does not initially settle out the suspended solids.

Screening

Large objects are removed at the pumping stations that force the sewage to the treatment plant.

Aeration

There are two aeration basins, each capable of handling five million gallons of sewage a day. Each basin is 474' long, 246' wide, and 15' deep; the capacity of each is ten million gallons

The raw sewage entering these basins is retained in them for forty-eight hours. During this time, eight mechanical surface aerators beat air into the water in each tank, thus providing oxygen for the growth of aerobic bacteria. The aerators are 100 H. P. electric motors that drive large propellers that cavitate the water, thus beating in air.

Supplied with adequate O_2, the aerobic bacteria do a remarkably effective job during the forty-eight hour period. Raw sewage having a B.O.D. of 312 is reduced to 43, which is about 86% reduction.

Settling

Following aeration, the waste goes to two settling tanks. These are 50' in diameter and 15' deep. They are similar to those described for the Wilmington plant.

The clear overflow of about five million gallons a day is then chlorinated.

The underflow is recycled to the aeration tanks. This also amounts to about five million gallons a day.

Chlorination

The overflow from the settling tanks has an average B.O.D. equal to 43; the goal is 30. Cl_2 is added in an amount sufficient to give 1 ppm of free Cl_2 after an hour. The clarified, chlorinated water is discharged into a nearby stream.

Aerobic Digestion

The reason for returning the underflow from the settling tanks to the aeration basins is to:

(a) add active bacterial cultures to the incoming sewage thereby facilitating its digestion;

(b) allow more time for the decomposition of biodegradable organic material.

There comes a time, however, when the biologically inert solids in the underflow build up to such an extent that recycling is no longer effective. If and when the suspended solids accumulate to about 5,000ppm, the sludge is then pumped to two aerobic digestors. These are 20' in diameter, and 30' deep; the capacity of each is:

$$3.14(10)^2 \times 30 \times 8.35 = 80,000 \text{ gallons}$$

The sludge remains in the digestion tanks for fourteen to twenty days, during which time the additional aerobic action completes the stabilization of the organic waste so that objectionable odors are minimized before the solids are hauled to a land fill.

For the above, air is provided by floating aerators. These are propellors driven by a 50 H.P. motor.

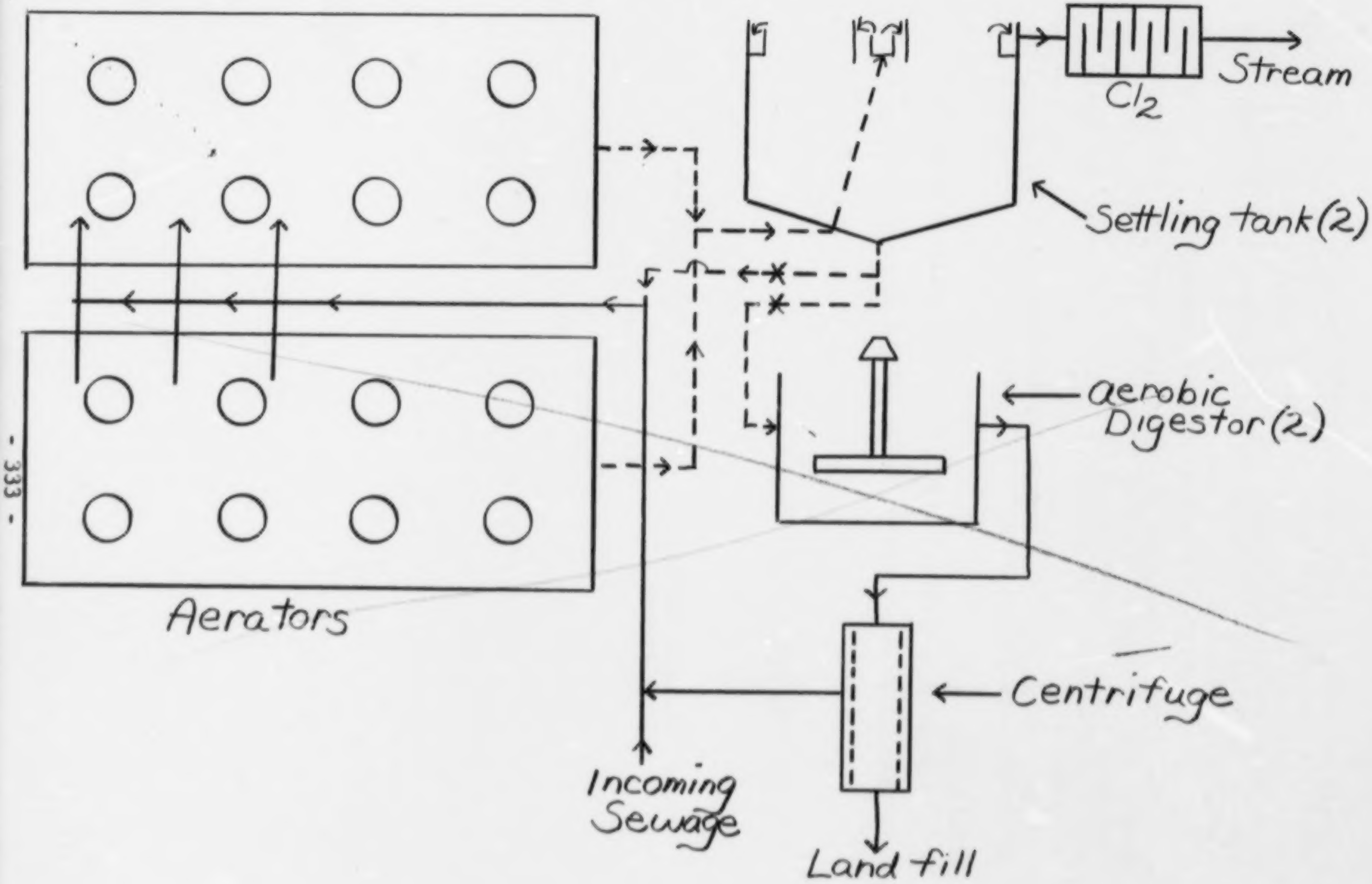
Exercise 9

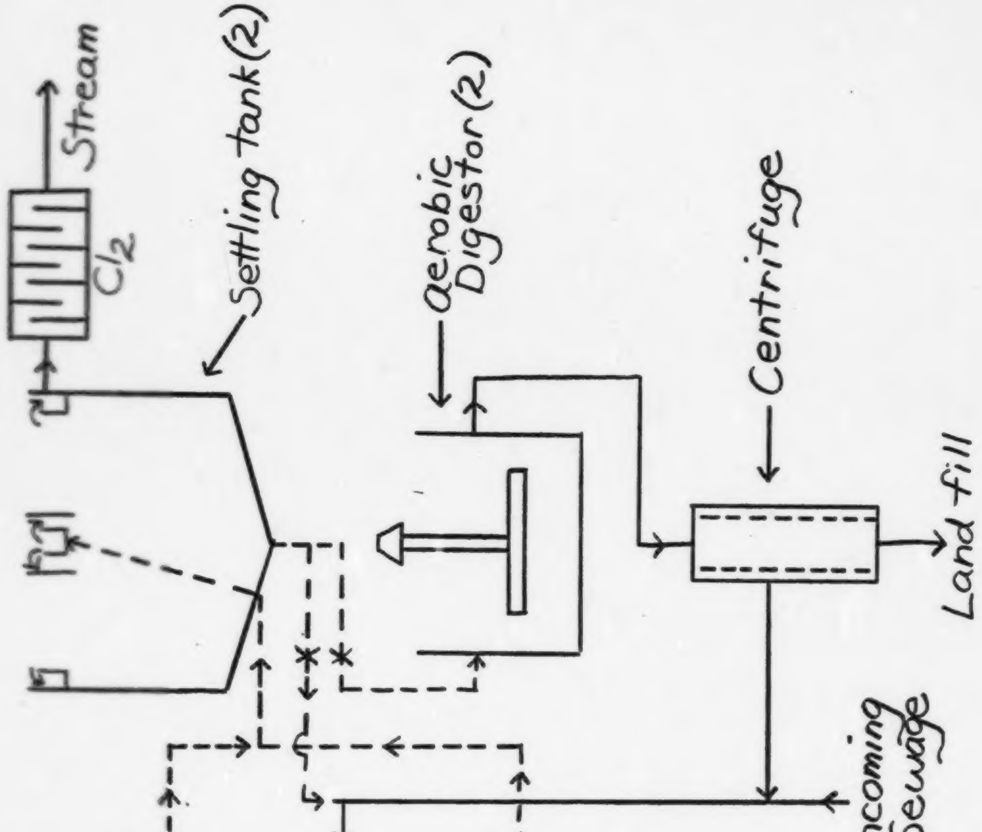
Suggest a possible source of the following problems?

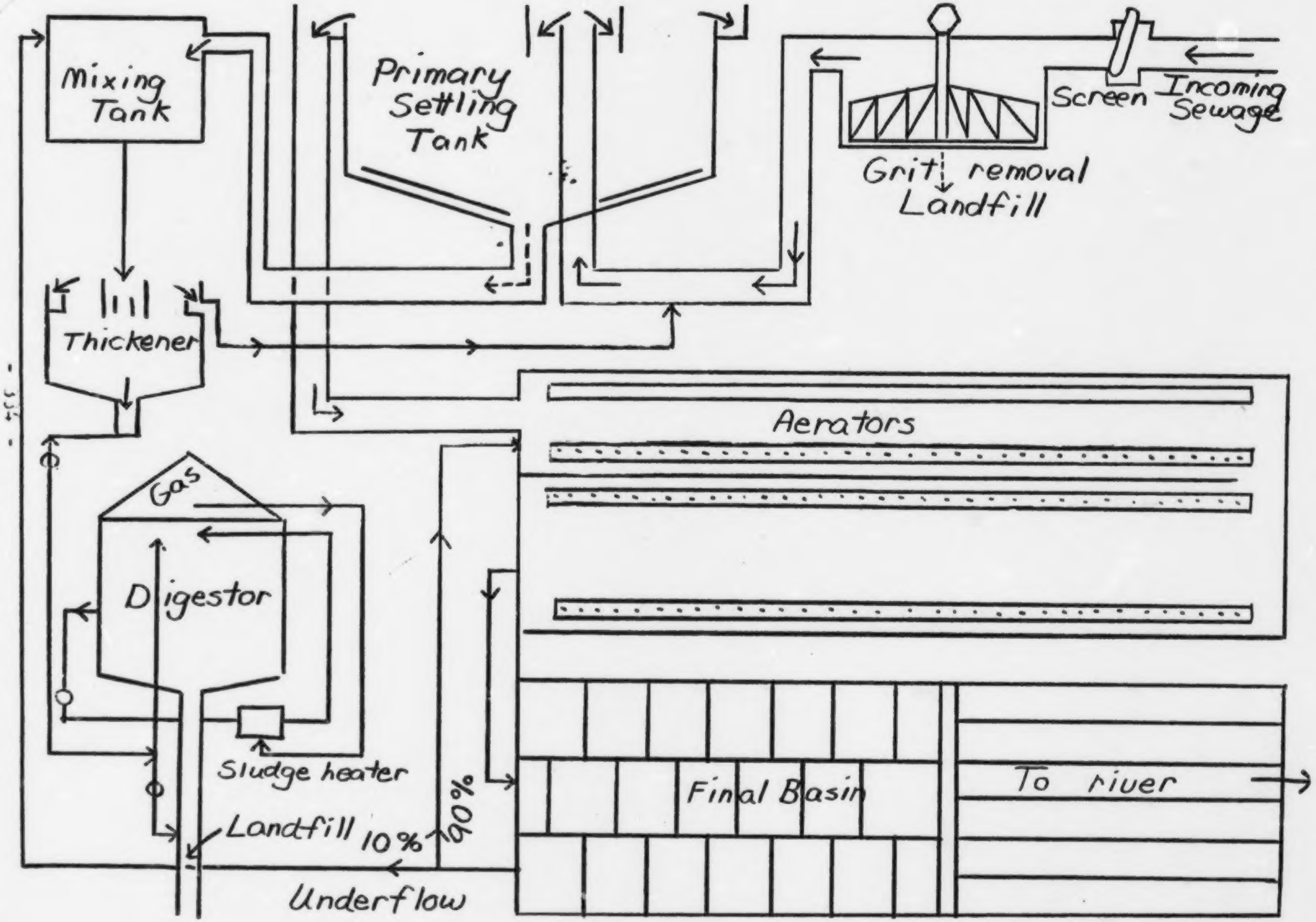
(a) Large metal objects clog up the aeration tanks.

(b) The final B.O.D. level is much too high.

(c) Harmful bacteria are found in the final water dumped in a stream.


Stream
Cl2
Settling tank(2)
aerobic
Digestor(2)
Aerators
Centrifuge
Incoming
Sewage
Land fill


Stream
Cl2
Settling tank (2)
aerobic Digestor (2)
Centrifuge
Land fill
Incoming Sewage
Aerators


Mixing Tank
Primary Settling Tank
Grit removal
Landfill
Screen
Incoming Sewage
Thickener
Aerators
Gas
Digestor
Sludge heater
Landfill
10%
90%
Underflow
Final Basin
To river

ANSWERS

Pretest

1. a) 1 gal. = 3.7853 liters = 3785.3g.

$3785.3 \times .0022046 = 8.345$ lbs.

12×10^6 gal. x 8.345 lb./gal. = 100×10^6 lbs./day

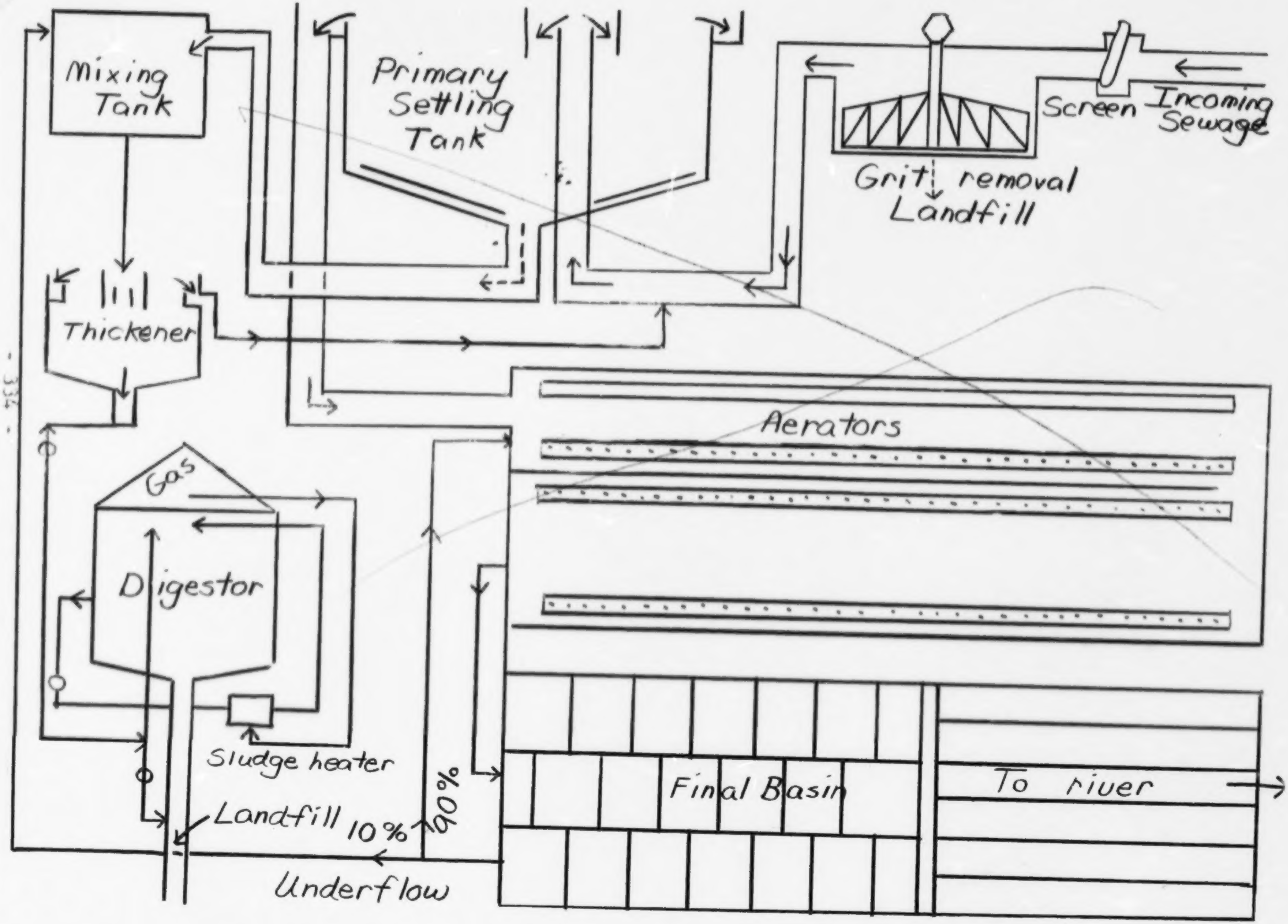
b) $300\times10^{-6} \times 100 \times 10^6 = 30{,}000$ lbs./day

c) $30{,}000 \times .8 = 24{,}000$ lbs./day

d) Discharged into a convenient lake, river or stream. Federal regulations now require that Cl_2 be added to such efficient water but many sewage plants are not yet equipped to do this.

2. Covered in text.

3. Covered in text.


Mixing Tank
Primary Settling Tank
Screen
Incoming Sewage
Grit removal
Landfill
Thickener
Aerators
Gas
Digestor
Sludge heater
Landfill
10%
90%
Final Basin
To river
Underflow

Study Guide

Exercise 1 & 2 - PRIMARY

This stage removes settleable solids (sludge) from the water. If a particular plant is not equipped for secondary treatment, the water is then discharged into a stream, lake or river; the solids may or may not be treated further.

Exercise 3 - SECONDARY

The water from the primary step is aerated, more solids settled out, chlorine added - or not, and the water discharged. The sludge from the above is digested, and the residue trucked to a land fill.

Exercise 4 - TERTIARY

This stage of treatment approaches the standards of a water purification plant. The effluent water from the secondary stage is chemically treated to remove some of the remaining dissolved solids and colloidal particles. The "polished" water is fit to drink. Though few plants do this today, it is a goal towards which the nation is moving; it is costly but may some day justify the price tag.

Exercise 5

No. This stage is needed to remove large particles which might interfere with further treatment procedures.

Exercise 6

Large particles could block openings or destroy the efficiency of the primary clarifier.

Exercise 7

Aeration adds oxygen to the water to facilitate the oxidation of biochemical materials.

Exercise 8

An amount is added which is sufficient to kill fecal coliforms; usually 4ppm of Cl_2 is sufficient.

Exercise 9

(a) Primary clarification not efficient.

(b) Incomplete aeration and/or insufficient time for bacterial action.

(c) Incomplete oxidation, poor aeration, insufficient chlorination.

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ANALYZING WATER

SUMMARY

This is not a mini-course, but an underlining of all the preceding mini-coursed.

The "bibles" of analytical techniques are:

1) "Standard Methods for the Examination of Water and Wastewater".
2) E.P.A.'s Manual, "Methods for Chemical Analysis of Water and Wastes".

No attempt has been made to list the most important tests versus those considered of less importance, solely because such a contrast cannot be made. It is up to the chemist to determine, in any given situation, what tests are needed and significant.

PREREQUISITES

In a sense, all preceding mini-courses have been aimed at preparing the student - both in theory and practical exercises - to understand the chemical tests he must be able to make; that is, for the job of analyzing water.

ANALYZING WATER

The "bible" of water analysis is "Standard Methods for the Examination of Water and Wastewater" prepared and published jointly by the:

American Public Health Association
American Water Works Association
Water Pollution Control Federation

The procedures described in this rather large book are varied and many; cross reference are frequent and often confusing; the book itself is hard to come by; some of the tests are included on a tentative basis and thus not officially accepted; of particular importance, the E.P.A. does not approve and use all of the procedures contained in Standard Methods. For these reasons, it was considered advisable to provide the student with a copy of E.P.A. approved procedures: "Methods for Chemical Analysis of Water and Wastes".

No attempt has been made to list the tests that might be required of the chemist, except the ones of almost universal concern - such as B.O.D., C.O.D., various compounds of nitrogens - which are described in detail in preceding mini-courses.

Chemical analytical techniques are becoming more and more sophisticated with ever increasing emphasis on automatic equipment and highly sensitive instruments. There will be found in the well equipped laboratory specializing in the analysis of water: expensive and delicate spectrometers, gas chromatographs, atomic absorption spectrometers, specific ion electrodes and meters, mass spectrometers, computers; conductivity cells and meters, pH meters, Kjeldahl equipment, soxhlet extractors, incubators, microscopes, furnaces; a complete assortment of glassware and conventional analytical apparatus.

With all the above - and more - at his command, the water chemist must be able to trust his results. This means frequent cross-checks and standardization against solutions of known content. Turning out results that are erroneous can be more misleading than no data at all.

The procedures approved by the E.P.A., some of which are contained in Standard Methods, are being constantly checked and revised to insure accuracy, dependability and the utilization of new analytical equipment and techniques. Even so, in any given situation, the chemist is frequently confronted with an unusual situation which necessitates his special attention. For example, an accidental acid spill may kill the bacteria in a sewage treatment plant, or phenolic contaminates may impart offensive odors and tastes to the purified water serving a large city. What to do, what tests to run, and how to quickly cope with such situations requires more experience than can be found in any book.

The chemist and the administrator must beware of pot-boiling and wheel-spinning. In other words, the appearance of being busy for appearance's sake. There is no value in running tests that are meaningless, or have long since served their purpose. Constant vigilance and periodic review by the chemist will pay handsome dividends in saved time and improved efficiency, if the contents of a report are scrutinized with the intent to eliminate tests which are no longer of interest or value to anyone.

This mini-course completes the series but, hopefully, is not the end but the beginning of the students' interest in water chemistry. The material covered has deliberately stressed fundamental principles for, with these mastered, the path is open for the comprehension of the new techniques and instruments that are being brought constantly to the attention of the water chemist. Just make sure that the innovation is sound, worth the investment, and acceptable by the E.P.A. and/or Standard Methods.